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PROCEEDINGS OF

THE ROYAL SOCIETY.

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An Experimental Determination of the Critical Electron Velocities for the Production of Radiation and Ionisation on Collision with Argon Atoms.

By Frank Horton, Sc.D., Professor of Physics in the University of London, and Ann Catherine Davies, M.Sc., Royal Holloway College, Englefield Green.

(Communicated by C. T. R. Wilson, F.R.S. Received September 29, 1919.)

In the 'Proceedings of the Royal Society' for 1919 (A, vol. 95, p. 408) we have given an account of an investigation of the effects of electron collisions with helium atoms. The apparatus and method there described have been somewhat modified, and applied to a similar investigation with argon. With this gas Franck and Hertz* came to the conclusion that ionisation occurs when the velocity of the colliding electrons is raised to 12 volts, but the method of experimenting used by them was not able to distinguish between ionisation of the gas and the photo-electric effect of radiation produced by the collisions.

The main features of the apparatus used in the present research† have been described in the earlier paper; the modifications introduced will be seen by reference to the diagrammatic view in fig. 1. A short tungsten filament, F, which could be heated to incandescence by an electric current, was used as the source of electrons. This was supported horizontally and about 1·5 mm. below the top of the platinum thimble, E, which was plane and circular, and had at its centre a circular hole 1·5 mm. in diameter.

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* J. Franck and G. Hertz, 'Deutsch. Phys. Ges. Verh.,' vol. 15, p. 34 (1913).

† I am indebted to the Government Grant Committee of the Royal Society for the means of purchasing some of the apparatus and materials used in this research.—F. H.

The platinum thimble was made out of thin sheet, and just fitted into the lower glass tube of the apparatus. Thus electrons from the glowing filament could only get into the ionisation chamber through the small hole, and it was hoped that this device would approximate to an equipotential source by limiting the effective emission to that coming from a small area at the middle of the filament. In the figure, D, C, N, and B are circular pieces of fine platinum gauze, of which N has been introduced since the earlier experiments with helium. In order to make the beginning of ionisation and radiation well marked, even at low pressures, the space in which these can occur was made larger in the present investigation, the distance between the gauzes C and N being 3 cm., as compared with a corresponding distance of 1 cm. in the earlier experiments. As before, the collecting electrode A was of platinum, and was suspended inside a platinum cylinder, within which it could be raised or lowered over a range of several centimetres. All the platinum used in the apparatus was carefully cleaned by boiling for many hours in strong nitric acid before being fitted into position.

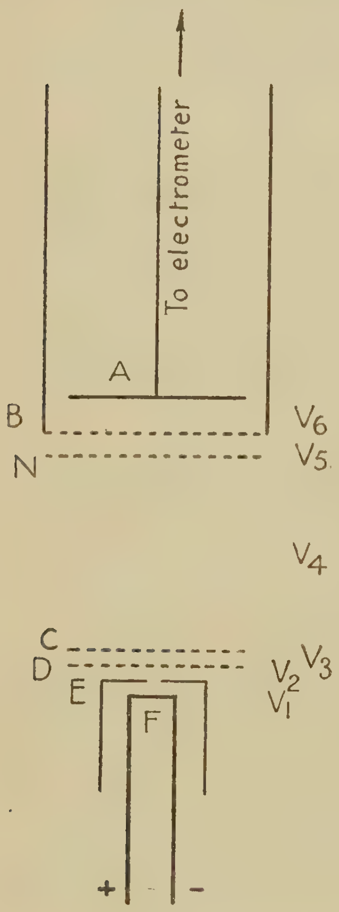

Fig. 1.

The two gauzes C and D were used in addition to the platinum thimble, E, in order to keep the emission from the filament constant as the voltage accelerating the electrons into the ionisation chamber was increased, and also to limit the range of velocities among the electrons employed. To this end a constant accelerating potential difference, V_1, was applied between the negative terminal of the filament and E, and a constant *retarding* potential difference, V_2, a little less than V_1, was applied between E and D. Thus, if the screening effect of the gauzes is complete, the same number of electrons, with the same velocities, should reach the gauze D however the fields above this gauze are varied. The variable part of the accelerating voltage (V_3) was applied between the gauzes D and C which are 2 mm. apart. In some of the later experiments it was desired to have a larger electron current through the ionisation chamber without unduly raising the temperature of the filament, and in these experiments a small constant accelerating field was used between E and D instead of the retarding field mentioned above, so that the full emission from the middle of the filament was used.

As in the experiments with helium, the apparatus was wrapped round by many turns of wire, through which an electric current of from 1·5 ampères to 2·0 ampères was sent during the observations. In this way a strong magnetic field parallel to the axis of the tube was produced, which prevented the stream of electrons from spreading laterally.

The argon supplied to us contained about 15 per cent. of nitrogen. This was removed by sparking between platinum electrodes with an excess of oxygen. During this process the gases were enclosed over a solution of potash in water, and oxygen was obtained as required by electrolysis of the water. The sparking was continued for about 100 hours after the volume of the gas had become constant, and the excess of oxygen was finally removed by heating spirals of copper wire in the mixed gases. Some of the argon was then drawn off by means of a stopcock into a highly exhausted glass globe, which it entered through a **U**-tube immersed in solid carbonic acid, so as to remove the water vapour from the gas. The glass globe was then sealed off, and the argon it contained was used in the first experiments. By turning a stopcock, it was allowed to pass along a fine capillary tube, from which it entered the apparatus, at the level of the gauze C, through a **U**-tube immersed in liquid air. The argon remaining in the sparking tube was again sparked with oxygen for a period of three weeks. The excess of oxygen was then removed by phosphorus, and the argon was transferred to a second storing vessel and used in the later experiments. Similar results were obtained with the two specimens, from which it may be concluded that both specimens were pure. The spectrum of the gas was observed by means of a small vacuum tube attached to the apparatus. Only the argon lines were visible, but the spectroscopic test is not a very delicate one, for we were unable to detect nitrogen spectroscopically in a sample of argon which contained 3 or 4 per cent. of nitrogen.

Before beginning the experiments, the apparatus was pumped out by a mercury vapour pump and the residual gas removed as completely as possible from the filament, electrodes, and glass walls of the apparatus, by long-continued heating and pumping. During the observations, argon was slowly streaming through the apparatus, the pressure of the gas being adjusted both by the tap on the storage bulb and by the pumps. As a series of observations usually occupied about an hour, it was impossible to maintain the pressure constant throughout, but the variations in pressure were not large and they were gradual—a steady increase or decrease, according as the pump was working too slowly or too quickly; thus no discontinuity was caused in the curves obtained.

Preliminary Experiments to Obtain Approximate Values of the Critical Electron Velocities.

In these experiments the fields V_1 and V_2 were constant, and the energy with which the electrons reached the level of the gauze C was varied by increasing the accelerating field V_3. The gauzes C and N were connected together so that, unless loss of energy by collisions with argon atoms occurred, the electrons would maintain the velocity they have at C over the distance C N. Thus when the velocity reaches a critical value an electron is able to produce radiation or ionisation if it collides with an argon atom in this space. As the distance between C and N is 3 cm. a considerable effect should be produced even at pressures as low as 0·01 mm., for most of the electrons entering the space C—N would make collisions with argon atoms. The electrons which pass through the gauze N encounter an opposing electric field, sufficiently strong to prevent any of them from reaching the gauze B, so that none can pass to the plate A, and the electrometer should therefore give no indication of a current until the collisions with argon atoms in the space C—N give rise to either radiation or ionisation. The method used to distinguish between these two effects is that used by Davis and Goucher* in their experiments with hydrogen and other gases, and by ourselves in the experiments with helium. It consists in observing the effect of reversing the direction of the small difference of potential V_6 between the gauze B and the collecting electrode, A, and thus reversing the current in this space due to the photo-electric action of any radiation which is produced by the electron collisions.

It must be noticed that since the field V_4 between the gauzes C and N is zero, the detection of ionisation by collisions in this space depends upon the positive ions formed diffusing into the space above the gauze N. Those which do so will be driven by the field V_5 towards the collecting electrode, but they may be retarded or even prevented from reaching it by the field V_6. If the gauze B is charged negatively to the plate A, radiation acting photo-electrically upon B will cause the electrometer to indicate a negative current. A field between B and A in this direction will, however, tend to retard any positive ions which pass through the gauze B, but, provided this field, V_6, is small, and the pressure of the argon not too high, the positive ions should be able to reach the collecting electrode against the retarding field. Thus, with this arrangement of the fields, the electrometer should indicate a positive or a negative current according as the effects of ionisation or those of radiation predominate. Series of observations of the current to the collecting electrode with different accelerating voltages, taken with the gauze B at a negative potential compared with the plate A, will be referred to as (I − R) series. If the gauze B is at a positive potential compared with the collecting electrode, positive ions getting through this gauze will be further accelerated towards that electrode by the field V_6, and since the photo-electric effect of any radiation produced will now tend to make the plate A lose electrons, both radiation and ionisation will tend to cause the electrometer to indicate a positive current. For this reason curves obtained from observations with B positive to A will be referred to as (I + R) curves.

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* Davis and Goucher, 'Phys. Rev.,' vol. 10, p. 101 (1917).

Typical examples of (I − R) curves are given in curves I and II of fig. 2. Both sets of observations showed a negative current beginning between 9 and 10 volts accelerating potential difference. This indicates that when the applied accelerating potential difference reaches this value, the electrons have sufficient energy to produce radiation on colliding with the argon atoms. It will be seen that the negative current due to radiation increases steadily until the point marked A on each curve; at these points the increase ceases and the negative current begins to decrease, showing that at this stage positive ions are reaching the collecting electrode. It will be observed that the accelerating voltage at which this change occurs is very different in the two curves given. In curve I it is 16·4 volts, while in curve II it is 14·4 volts. The main difference in the conditions under which the two curves were obtained is that in the case of curve I, the pressure of the argon gradually rose from 0·078 mm. to 0·099 mm. during the observations, whereas in the case of curve II the pressure measured by the gauge was much lower varying from 0·00197 mm. to 0·00175 mm. during the experiment. In both cases the distance of the collecting electrode A, from the gauze B, was 1 cm., and the difference in the positions of the point A on the two curves is no doubt explained by the greater difficulty experienced by the positive ions in reaching the plate at the higher pressure. These curves may, therefore, be taken as indicating that collisions resulting in radiation first occur when the potential difference accelerating the electrons has a value between 9 and 10 volts, and that ionisation of the argon is produced when this potential difference is increased to about 14·4 volts. In other experiments the presence of positive ions was detected with accelerating voltages slightly less than this, so that it is probable that even in the case of curve II, positive ions are not reaching the collecting electrode until the velocity of the electrons has been raised above the value at which they are first formed.

Another point to which attention must be called is the sharp upward bend in curve I at the point marked B. The observations recorded in this curve are plotted on a smaller scale in curve I′ which gives a better idea of the relative magnitudes of the changes which occur at the points A and B. The upward bend at B indicates a sudden increase of positive current and this

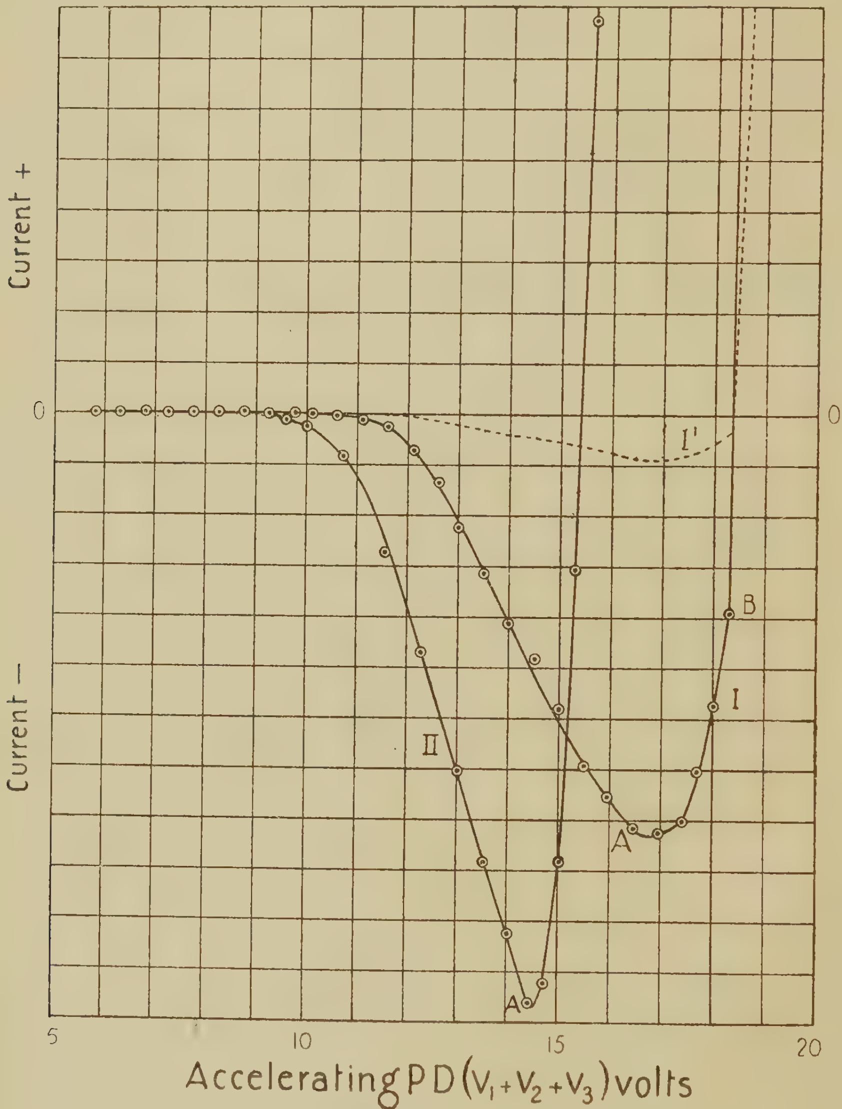

Fig. 2.

change was always preceded by an unsteadiness of the measured current, that is to say, repeated observations under apparently the same conditions were not in good agreement. In some (I − R) curves, taken at higher pressures, the bends at A and B were not so distinctly separated as in curve I. In some instances A and B coincided, and the current changed abruptly from an increasing negative current to a relatively enormous positive current, while in other curves obtained the point A was marked merely by a discontinuity in the negative current and was separated from B by a small fraction of a volt only. A more complete investigation of this effect is recorded in a later section of the present paper.

Fig. 3 represents a series of measurements of the (I + R) currents taken with the collecting electrode about 0·5 mm. from the gauze B. Argon was,

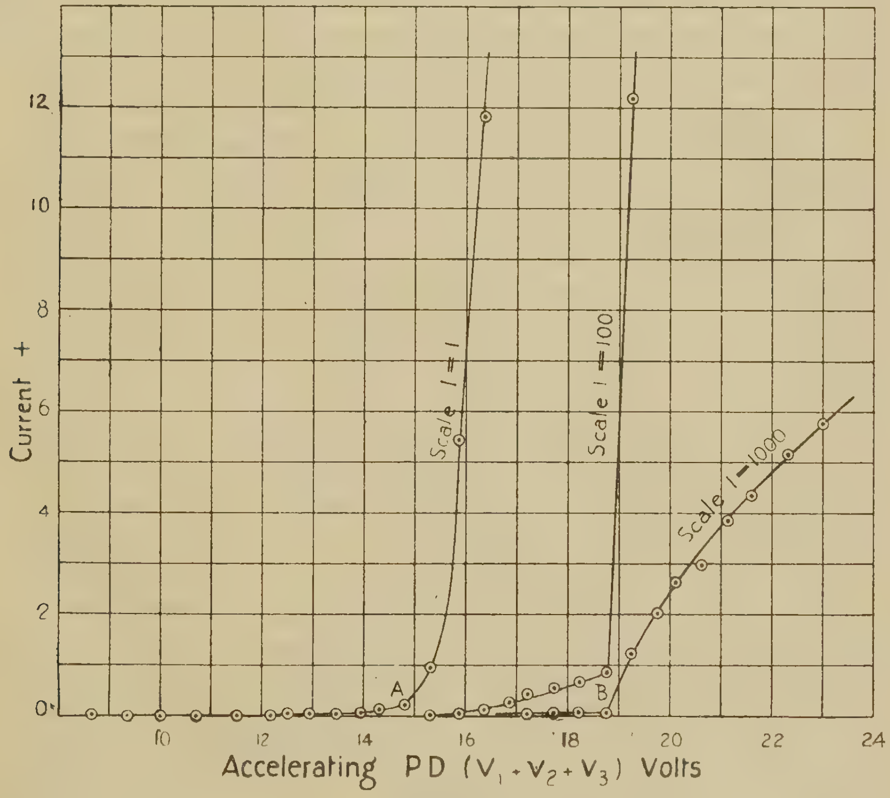

Fig. 3.

as usual, streaming through the apparatus during the observations and the pressure increased gradually from 0·026 mm. 0·031 mm. during the series. In order to show the relative magnitude of the sudden changes in the measured currents the latter are plotted on three different scales which are marked on the curves. The gradual increase in the positive current at the lower voltages is due to radiation. The point A corresponds to the point A in the (I−R) curves and indicates that positive ions due to ionisation of the argon are beginning to be collected. In the curve given the bend is at about 14·8 volts. A second sharp bend indicating a large increase in the positive current occurs at B which corresponds to the point similarly marked in the curves of fig. 2. It was found that the positions of the two bends A and B varied considerably in different experiments, even in the (I+R) series of observations, so that the arrangement of fields in which $V_4 = 0$ is not a satisfactory one for detecting the beginning of ionisation by collision. This is perhaps to be expected for when V_4 is zero, the detection of ionisation depends mainly on the positive ions formed diffusing out of the space between the gauzes C and N into the space above the latter gauze It seemed possible that the test for positive ions might be improved by establishing a difference of potential between the gauzes C and N so as to drive positive ions formed in this space through the gauze N, and thus towards the collecting electrode A. Such a field would, of course, retard the electron stream from the filament and would therefore limit the range over which the production of radiation and ionisation could occur when the critical accelerating voltages were reached. This diminishes the amount of radiation or ionisation and so renders the test for radiation less sensitive, but experiments showed that the diminution in the amount of ionisation was more than counterbalanced by the greater proportion of the positive ions formed which were driven to the collecting electrode.

Fig. 4 gives examples of (I−R) and (I+R) curves obtained with a difference of potential of 36 volts between the gauzes C and N. The values of the current are plotted on two scales, the currents in the dotted curves being on one-tenth the scale of the others. At each value of the accelerating voltage (I−R) and (I+R) observations were taken consecutively thus avoiding a difference in the form of the two curves which might arise from any variation of the electron stream, or of the gas pressure. With a potential difference as large as 36 volts opposing the electron stream in the space C—N, the production of radiation (and of ionisation) is restricted to a layer of gas close to the lower gauze C and it will be seen that the photo-electric effect of the radiation on the plate A or on the gauze B was not detectable, for there is no rise in the (I+R) curve, nor fall in the (I−R) curve when the accelerating potential difference is about 10 volts, at which point we have already seen that radiation is produced. An increase in the measured positive currents occurred in both the (I+R) and the (I−R) observations when the accelerating voltage was raised from 13·1 volts to 14·6 volts, showing that ionisation begins between these limits. These observations were taken with argon streaming through the apparatus at an average pressure of 0·020 mm. The field V_4 in this experiment was sufficiently large to prevent any of the electrons from the filament from reaching the collecting electrode; the field V_5 was in the same direction, the difference of potential between the gauzes N and B being 23 volts. Thus, as soon as ionisation occurs, the positive ions are accelerated towards the gauze N and those which pass through this

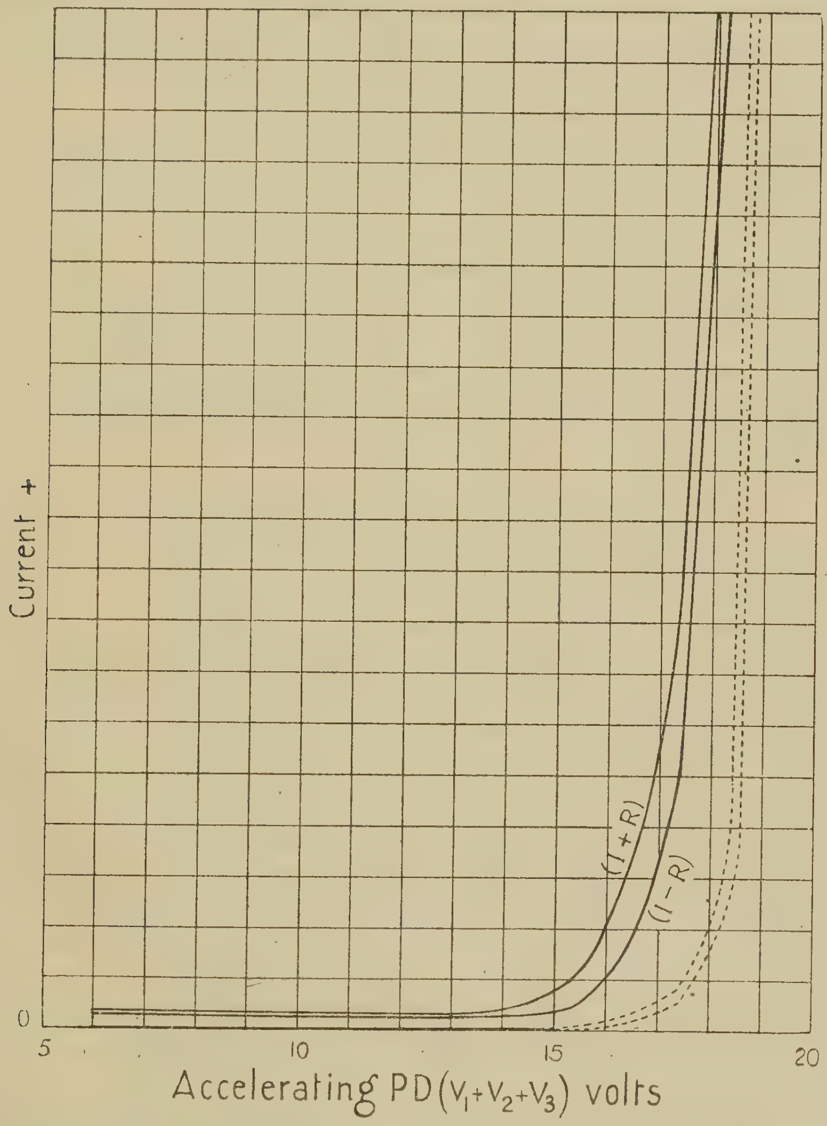

Fig. 4.

gauze are further accelerated towards the gauze B. The velocity of the positive ions driven through B should therefore be sufficient for them to travel the small distance separating the plate A from the gauze B (5 mm. in this experiment) even in the case of the (I − R) observations in which the difference of potential V_6 (1·5 volts) opposes them. Under these conditions, therefore, an increasing positive current should be detected as soon as the velocity necessary for ionisation by collisions is reached.

The velocity of the swiftest electrons getting through the gauze C under a given applied accelerating potential difference was determined under the conditions of experiment in which the curves in fig. 2 and fig. 4 were obtained, and it was found in both cases that the fastest electrons had a velocity corresponding to a potential difference 2·0 volts greater than the applied accelerating voltage. The minimum radiation velocity determined from the curves of fig. 2 is thus between 11 and 12 volts, and the minimum ionisation velocity determined from the curves of fig. 4 lies between 15·1 volts and 16·6 volts.

The Exact Determination of the Critical Velocities.

In order to determine as accurately as possible the value of the miminum velocity an electron must have in order to produce radiation on collision, the two gauzes C and N were connected together so that, when the critical potential difference was reached, radiation might be produced throughout a considerable volume of the gas, and the effect to be detected made as large as possible. Further, in order to allow for any small variation in the natural leak of the electrometer system, or gradual change in the electron emission or the gas pressure, corresponding points on the (I + R) and (I − R) curves were obtained alternately. The point where these two curves diverged was taken as the value of the accelerating potential difference at which radiation began. Every series of observations from which a value of this voltage was determined was immediately followed by a determination of the correction to be applied to it, so as to obtain the velocity of the swiftest electrons present. Fig. 5 shows how well marked the divergence point could be made with this method of experimenting. The (I + R) and (I − R) curves clearly separate between the observations at 9 volts and 9·3 volts. After obtaining these curves, observations at voltages between 8·5 volts and 9·5 volts were repeated at intervals of 0·1 volt, and the point of separation was determined as 9·2 volts. The value of the correction was found to be + 2·2 volts, giving 11·4 volts as the minimum radiation potential difference. Many determinations of this point, under slightly different conditions of gas pressure and filament temperature, gave values ranging from 11·4 volts to 11·6 volts, and the mean of these, 11·5 volts, may be taken as the first critical velocity for electrons in argon.

In our paper on helium, we have described a method of determining the first critical potential difference which does not involve a correction for the velocity of emission of the electrons from the glowing filament. This method can be applied to any gas in which the collisions of electrons with the gas atoms are perfectly elastic when the electron velocity is below the critical value. In applying this method to the case of argon, the gauzes C, N, and B were all connected together and maintained at the same potential. The gas pressure has to be fairly high so as to make sure that no electrons pass through this space without colliding with an argon atom. Those electrons which get through the gauze B meet an opposing potential difference between that gauze and the collecting electrode. If, after

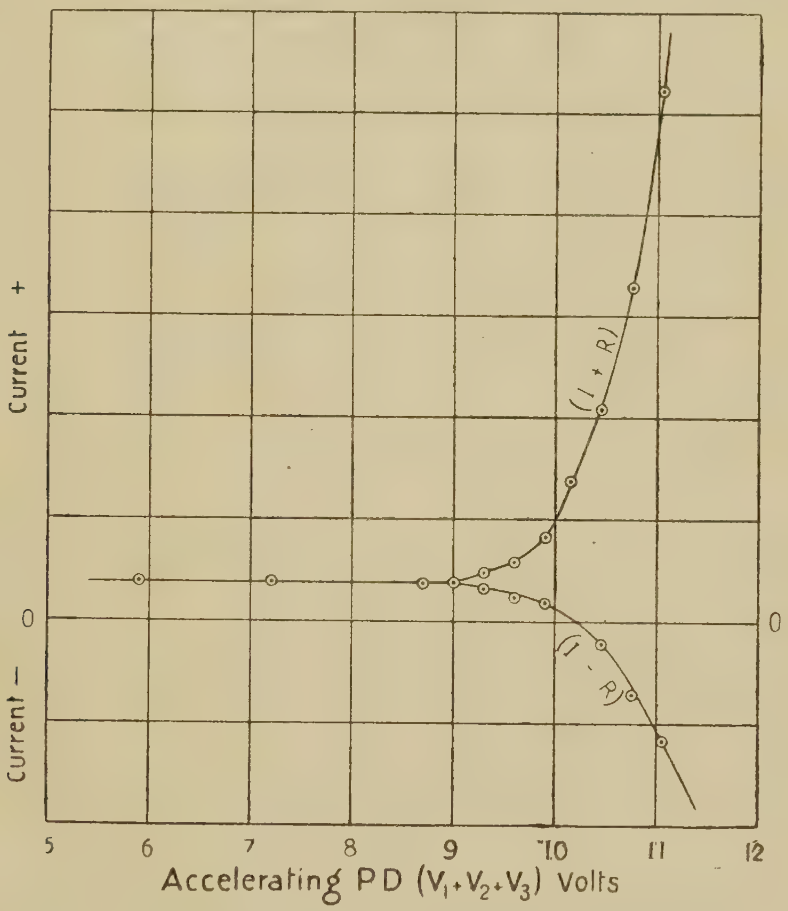

FIG. 5.

colliding with the argon atoms, they pass through B with a velocity greater than this opposing potential difference, they reach the collecting electrode, and cause the electrometer to indicate a negative current, but, if their velocity is less than this amount, they are completely stopped by the retarding field. It follows, therefore, that if this retarding potential difference, V_6, is fixed at some value less than the first critical potential difference, and the voltage accelerating the electrons is gradually increased, the latter will at some stage be able to get across to the collecting electrode, and a negative current will be detected. If, however, the difference of potential, V_6, is equal to the first critical potential difference for the gas, electrons with a velocity less than this will be unable to reach the collecting electrode, while, if the accelerating voltage is increased so as to be above this value, the electrons will lose most of their velocity by producing radiation from the argon atoms they collide with, and so will be still unable to reach the collecting electrode. The method of experimenting therefore consists in adjusting the difference of potential, V_6, until no negative current can be detected by the electrometer as the accelerating voltage is gradually raised. The lowest value of V_6 for which this condition holds gives the first critical potential difference independently of correction.

Experimenting in this way in the case of helium, results were obtained in good agreement with those given by other methods, but, in the present experiments with argon, the results were not so satisfactory. The difficulty appeared to be that, although the pressure was adjusted so that the distance between the gauzes B and C was several times the mean free path of the electron, nevertheless, some of the electrons entering this space with a velocity slightly greater than the minimum radiation potential difference were able to pass through it without losing energy, so that a retarding potential difference, V_6, greater than the critical voltage, was required to stop them. In these circumstances, the point at which the electrometer detects no current is that at which the number of electrons getting through to the collecting electrode is just equal to the number leaving that electrode owing to the photo-electric effect of the radiation from the argon atoms at which non-elastic collisions have occurred, and the value deduced as the minimum radiation potential difference from such an experiment will be higher than the true value. In the actual experiments with argon, at several different pressures, the values found ranged from 11·5 volts to 12·5 volts. From what has been written above it is probable that the lowest value obtained is most nearly correct, and, as was to be expected, it was obtained from the experiment at the highest pressure (about 1 mm.). These experiments may be taken as showing that, although an electron moving with a velocity of 11·5 volts is able to produce radiation when it collides with an argon atom, yet it does not always do so, but in some cases may even collide with several argon atoms in succession without appreciable loss of energy. We have recently made some experiments with helium which have shown that in that gas also, an electron moving with a velocity greater than that necessary to produce radiation may collide with a helium atom without loss of energy, but the experiments just described seemed to show that this effect is more marked in the case of argon.

An attempt was also made to obtain the value of the first critical potential difference for electrons in argon by a method similar to that employed by Tate and Foote* in their experiments with metallic vapours. The two gauzes B and N were connected together. The electrons from the filament were accelerated up to the gauze N and there was a small retarding field between the gauze B and the collecting electrode A. Fig. 6 is an example of the curves obtained on plotting the currents measured by the electrometer against the potential difference accelerating the electrons up to the gauze N. The curve slopes gradually downwards until the accelerating potential difference reaches 9 volts. At this point the swiftest electrons on colliding with the argon atoms produce radiation, thereby losing their velocity and being prevented by the small retarding field, V_6, from reaching the collecting electrode. As the accelerating potential difference is gradually increased beyond this point, more and more of the electrons lose energy in this way

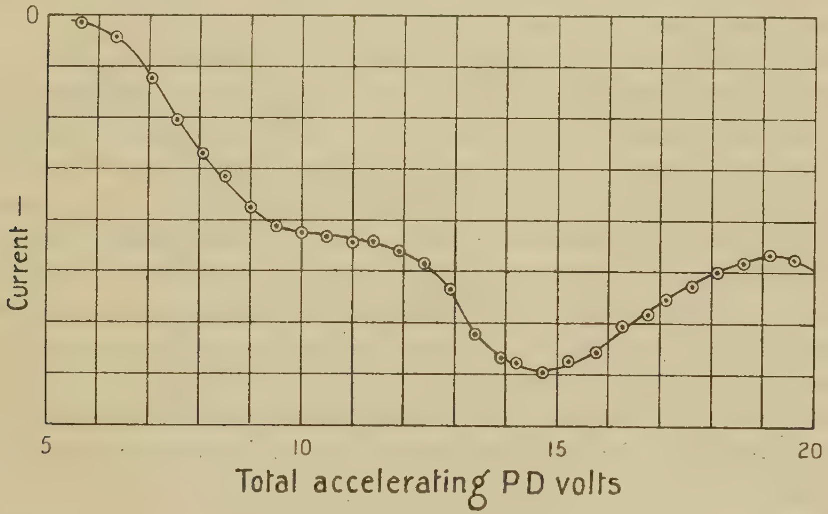

Fig. 6.

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* J. T. Tate and P. D. Foote, 'Phil. Mag.,' vol. 36, p. 64 (1918).

and the current curve does not turn downwards until about 11·5 volts is applied. Shortly afterwards, the downward slope of the curve decreases and leads to an upward bend, the point at which the decrease commences, 13·4 volts, indicating the point at which ionisation by collision begins. The average pressure of the argon during these experiments was 0·033 mm. The correction to be added to the applied potential differences in order to give the velocity of the swiftest electrons passing through the gauze N was found to be 2·2 volts. Thus the value of the minimum radiation potential difference for argon is 11·2 volts and the minimum ionisation potential difference is 15·6 volts as deduced from these observations. The position of the second critical point varied considerably in different experiments by this method, probably because the relative magnitudes of the various secondary effects produced by the electron stream depend upon the gas pressure and the arrangement of the electric fields used in any instance. On this account the results obtained by this method were not included in deducing the mean values of the critical velocities for electrons in argon.

The method used to determine accurately the value of the minimum ionisation potential difference was similar to that used in obtaining the results given in the curves of fig. 4. Series of (I + R) observations were taken with a potential difference V_4 of 20 volts or more between the gauzes C and N so as to drive any positive ions formed, through the gauzes N and B where the fields V_5 and V_6 drive them towards the collecting electrode, which for these experiments was lowered to within 1 mm. of the gauze B. When a positive current increasing with the accelerating potential difference is measured under these conditions, it may be due to three causes:—(1) To positive ions formed by ionisation of the argon atoms by electron collisions. (2) To the photo-electric effect of radiation from the argon upon the collecting electrode. (3) To positive ions liberated from the gauze C by the bombardment of the electron stream which is turned back upon it.

It has already been pointed out in connection with fig. 4 that when a considerable difference of potential is applied between the gauzes C and N, the photo-electric effect of the radiation on the collecting electrode, or on the gauze B, could not be detected. This enables us to neglect the second possible cause of the positive current referred to above. The absence of any detectable amount of radiation under these conditions also provides a means of distinguishing between a positive current due to cause (1) and a positive current due to cause (3). The energy with which the electrons, which are turned back in the space between the gauzes C and N, bombard the gauze C, will be smaller the longer the path they traverse in the gas. Therefore, if observations be taken simultaneously for two large values of the potential difference V_4, *e.g.*, 20 volts and 36 volts—the electrons being turned back to bombard the same gauze in each case—the measured positive current will be larger in the case of the 20 volts curve or in the case of the 36 volts curve according as it is due to ionisation of the gas, or to the liberation of positive ions from the gauze C.

In any particular series of observations, the approximate position of the point at which a positive current increasing with the accelerating potential difference began was first obtained for some value of the field V_4, and then further observations over that part of the curve were taken at intervals of 0·1 volt or 0·2 volt. These were immediately followed by a determination of the velocity of the swiftest electrons present when an accelerating potential difference slightly less than the critical value was applied. The correction obtained in this way was added on to the observed critical value and thus the minimum potential difference at which positive ions are produced was determined. A separate experiment was then made to investigate the origin of the positive ions at this voltage, by taking observations for two values of V_4, simultaneously, as already suggested. These observations showed that as soon as a positive current increasing with the accelerating potential difference was obtained, this current had a larger value when V_4 was 20 volts than when V_4 was 36 volts, thus indicating that increasing the path of the electrons in the gas increased the positive current, which must, therefore, be due to ionisation of the argon atoms and not to positive ions liberated from the gauze C. The minimum potential difference at which positive ions are produced, as already determined, is thus the minimum ionisation potential difference of the gas. Many such determinations were made at various pressures between 0·010 mm. and 0·040 mm. and with different values of the field V_4. The extreme values found for the ionisation potential difference were 14·7 volts and 15·4 volts but most of the values fell between 15·0 volts and 15·3 volts. The mean of all the values found was 15·1 volts, which may, therefore, be taken as the minimum ionisation potential difference for electrons in argon.

Experiments to Test for Ionisation at the First Critical Velocity.

The experiments already described have shown that radiation is produced when electrons moving with a minimum velocity of 11·5 volts collide with argon atoms, and that when the velocity of the colliding electrons is raised to 15·1 volts, ionisation of the gas occurs. From the results obtained by Franck and Hertz, it has hitherto been thought that argon is ionised by collisions of electrons having a velocity of about 12 volts. It therefore seemed desirable to make a further attempt to detect ionisation at the first critical potential difference, although the results already recorded show that if any ionisation does occur at this voltage, it is small in amount compared to that which takes place when the impacting electrons have a velocity of 15·1 volts. We were also influenced in making this further test by the fact that towards the end of the experiments described in the last section, trouble was experienced owing to polarisation layers forming on some of the gauzes. The presence of these was detected by the experiments to measure the velocity of the electrons under a given applied potential difference. It was also indicated by the points at which radiation and ionisation were first detected being delayed until the accelerating voltage had been raised several volts above the critical values previously found.

The special test for ionisation at the minimum radiation potential difference was made somewhat in the manner of the experiments by which the value 15·1 volts had been obtained for the minimum ionisation potential difference, but in view of possible polarisation layers the precaution was taken of obtaining two curves simultaneously, one to indicate the point at which radiation commenced, and the other to indicate the point at which positive ions were first detected. In obtaining the former, positive ions were prevented from reaching the collecting electrode, and the effects of radiation alone were studied. The ionisation curve was an (I + R) curve, with the conditions arranged so that the effects of radiation were very small. In order to make the test for ionisation as sensitive as possible, the method of having an electric field in the space between the gauzes C and N, so as to drive the positive ions towards the collecting electrode, was again used, and the collecting electrode was only 1 mm. from the gauze B. The results of one of these experiments, in which the average pressure of the argon was 0·022 mm., are shown in fig. 7. Corresponding points on the two curves were taken consecutively, so as to avoid any errors which might arise from a gradual change in the gas pressure or other conditions. The small positive current which was measured in the observations at the lowest voltages was indeed found to decrease slowly with the time, and this probably accounts for the gradual fall in the ionisation curve at the lower voltages. In both series of observations, the results of which are shown in the curves of fig. 7, the electron stream was turned back between the gauzes C and N, which were at a difference of potential of 18·7 volts. In the ionisation curve the potential differences, V_5 (1·4 volts) and V_6 (1·5 volts), were directed so as to drive positive ions towards the collecting electrode. It will be seen that the presence of these is first indicated between 15·0 volts and 15·8 volts. After each point on the ionisation curve had been determined, the point for the same accelerating potential difference on the radiation curve was found. This was done by reversing the direction of the difference of potential between the gauzes B and N (V_5), and increasing it so as to prevent positive ions, passing through N, from reaching B. The small field V_6 was also reversed, so that the effect of radiation would be to produce a negative current by acting on the upper surfaces of the gauzes B and N. The effect of the radiation on the upper surface of the gauze B alone has been shown by earlier observations to be very small, except when the field V_4 is very small, but the electrons liberated photo-electrically from the gauze N gave a considerable effect, as can be seen from the radiation curve in fig. 7. The radiation curve diverges from the ionisation curve at about 11·5 volts, which is therefore the point at which radiation begins in both series of observations. The ionisation curve shows no increase of positive current at this point, nor indeed until the accelerating potential difference is raised above 15 volts. There is thus no detectable amount of ionisation of the gas produced at the first critical velocity.

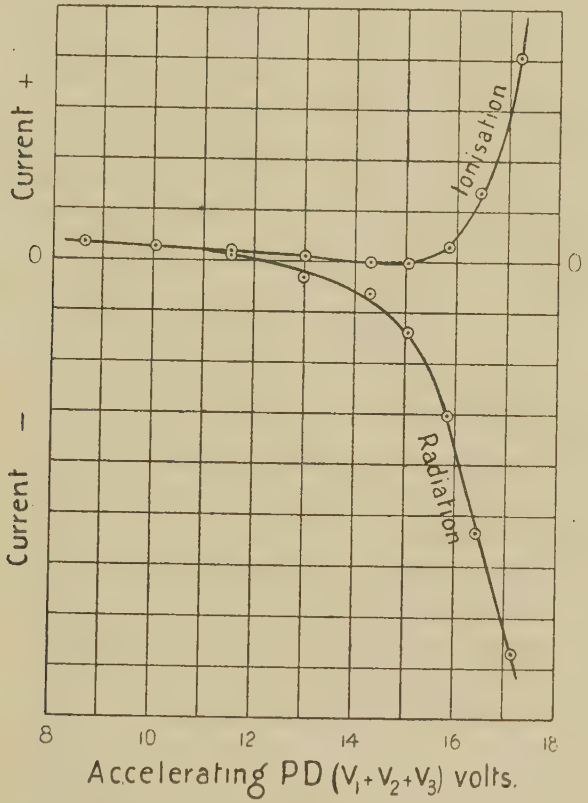

Fig. 7.

An Investigation of the Relatively Large Increase of Current which Occurs a few Volts above the Minimum Ionisation Potential Difference.

In an earlier section of this paper we have pointed out that when the velocity of the electron stream was increased a few volts above the ionisation potential difference, a large increase occurred in the positive current measured by the electrometer. This is well illustrated in Curve I′ of fig. 2. This effect was most marked in those series of observations which were taken with $V_4 = 0$, and it was found that on repeating the observations with gradually decreasing values of the accelerating potential difference, after the sudden increase of current had occurred, the resulting curve did not coincide with the curve for increasing values of the accelerating potential difference. The exact form of the curve obtained depended on the conditions of experiment. Fig 8 shows an (I—R) curve taken with an average pressure of 0·0014 mm. of argon in the apparatus, and with no potential difference between the gauzes

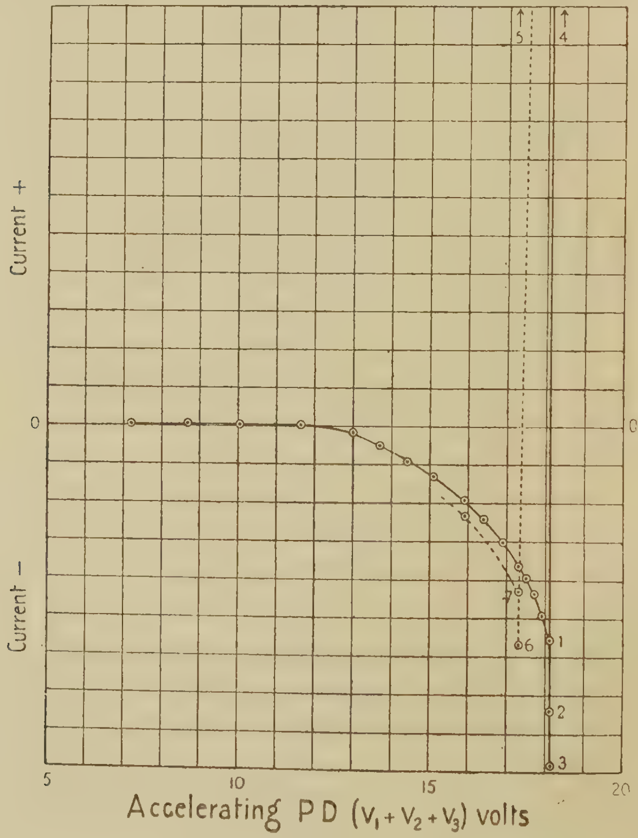

FIG. 8.

The numbers 1–7 refer to the order in which the points were obtained.

C and N. This curve shows that the negative current measured became characteristically unsteady at the accelerating potential difference at which the increase in positive current occurred. The dotted curve represents the currents measured on gradually decreasing the accelerating potential difference. It will be seen that the current remained positive for some time, decreasing with the accelerating voltage to a maximum negative value. Keeping the accelerating potential difference constant, the magnitude of this negative current quickly decreased with time until the measured value became about the same as that observed for the same accelerating voltage on the outward path. The indication of a sudden increase in the radiation at the points 1, 2, 3, in fig. 8 was further investigated by obtaining two curves simultaneously—(*a*) an (I—R) curve, showing the effects of the positive ions, and (*b*) a curve showing the effects of the radiation only. The latter was obtained from a series of observations under conditions in which no positive ions could reach the collecting electrode. The resulting curves are shown in fig. 9. In all the observations the field V_4 was zero, and the electrons from the glowing filament were turned back by the field V_5. In the (I—R) curve, V_6 was 3 volts, while in the radiation curve V_6 was 36·2 volts, the gauze B being negative to the collecting electrode in both cases. Thus in the radiation experiment no positive ions could reach the collecting electrode. The (I—R) curve is similar to those already given and shows the occurrence of radiation, then ionisation, and finally a big increase in the positive current between 20·0 volts and 20·2 volts accelerating potential difference. In the radiation curve the currents are negative all the time, and it will be seen that an enormous increase in the negative current occurs at the same point as that at which the increase in the positive current occurs in the (I—R) curve. Evidently in the latter curve the large effect of radiation is more than counterbalanced by the increased number of positive ions which is collected.

The largely increased current which is obtained in these experiments is similar in its magnitude, in the suddenness with which it takes place, and in the hysteresis which the large current then shows with regard to the accelerating potential difference, to the increase which occurs under certain circumstances when a glowing cathode is used in an evacuated tube with a single anode. This effect was observed some years ago,* and it was found that under the usual conditions the large increase of current across the tube coincided with the appearance of luminosity in the residual gas present. In the present experiments it was found that the sudden increase in the current was accompanied by a faint glow in the gas between the gauzes C and N.

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* F. Horton, 'Phil. Trans.,' A, vol. 207, p. 147 (1907).

This glow increased in brightness as the accelerating voltage was increased further, but it was always very faint, especially at the lowest pressures.

The sudden increase in the ionisation of the gas and the accompanying luminosity is a phenomenon of considerable interest. A simultaneous increase of radiation and of ionisation might be explained by a sudden neutralisation of the space charge effect, which is due to the mutual repulsion of the electrons preventing the maximum emission from the glowing filament.

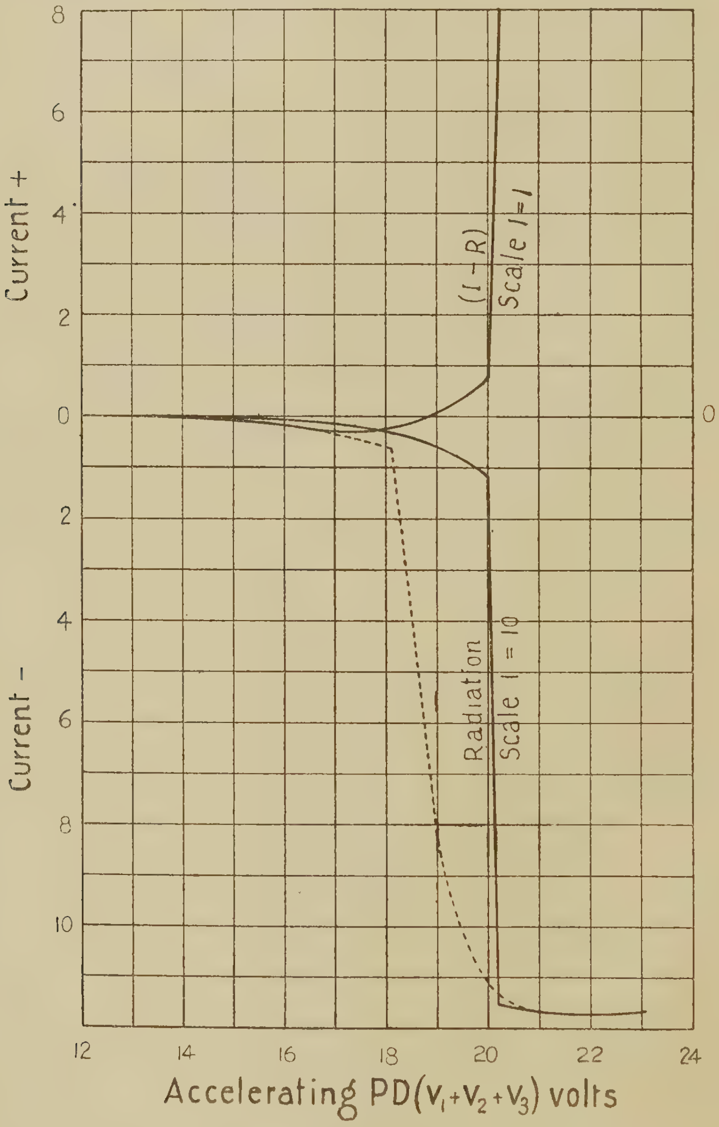

Fig. 9.

The effect of this is considerable only when the cathode is very hot and the emission large, but it is under such conditions that the sudden appearance of the gas luminosity is most marked.

The fact that the sudden increase in the positive current does not begin until a few volts after the electrons are able to ionise the gas, seems to indicate that it is necessary for a certain proportion of positive ions to reach the filament before any considerable neutralisation of the space charge effect and consequent increase in the emission takes place. Evidence of the correctness of this suggestion was provided by the fact that the conditions of experiment which are most favourable to the presence of a considerable number of positive ions near the filament are those under which the lowest values were obtained for the applied potential difference at which the large increase of positive current was observed. On the view that a certain proportion of positive ions is necessary to cause the effect, the hysteresis which the largely increased current shows with respect to the potential difference accelerating the electrons is also explained, for the increased emission will result in an increase in the number of positive ions present; thus as the applied accelerating voltage is reduced neutralisation will continue until the number of positive ions produced by the increased emission falls below that required to maintain the neutralisation.

It must, however, be pointed out that an increased emission of electrons from the filament, however produced, is not sufficient to account for the sudden change of the measured current from a large negative value to a very large positive one, as was often obtained in the (I—R) series of observations. It seems possible that some other factor comes in which increases the proportion of the electrons making ionising collisions at this point. The most obvious of such possible causes is the radiation which is being produced in the gas. Some experiments of Hebb with mercury vapour* make it appear improbable that the radiation produced from a gas acting photo-electrically on the atoms of that gas can ionise them, and such a result is definitely disproved for argon by the experiments we have described, showing that there is no detectable amount of ionisation when radiation is first produced, but it is not impossible that when the accelerating potential difference has reached the minimum ionising value, the proportion of the collisions between electrons and argon atoms resulting in ionisation of the gas is increased when the atoms are exposed to intense 11·5-volt radiation. From the curve of fig. 8, which is typical of many observations of the current in (I—R) experiments, it may be seen that the immediate consequence of the increased emission due to the neutralisation of the space charge effect is an increase of negative current due to radiation. The fact that this increase precedes the detection of the very large positive current which is ultimately measured at the same voltage, supports the suggestion that the radiation itself is a contributory cause of the increased ionisation.

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* T. C. Hebb, 'Phys. Rev.,' vol. 11, p. 170 (1918).

Another possible cause of the greatly increased ionisation of the argon which occurs a few volts above the minimum ionising potential difference, is that a radiation capable of ionising the gas directly may be produced. Sir J. J. Thomson has been able to detect the production of soft Röntgen radiation by the impact of cathode rays with velocities as small as 10 volts.* In the present experiments it is unlikely that the large increase in current is due to a radiation requiring a definite minimum velocity of electrons for its production for the applied potential difference at which the large increase of current occurred varied in different cases from 17 volts to 21 volts. Moreover, if the effect were due to an ionising radiation we should expect to measure larger currents when the collecting electrode was raised some distance above the gauze B than when that distance was very small, but no result which could be attributed to such an effect was observed.

Discussion of Results and Conclusion.

The experiments described in this paper have shown that, when electrons bombard argon atoms, a radiation is first produced from the gas, when the electrons attain a velocity of 11·5 volts, and that ionisation of the gas occurs when the electron velocity is further raised to 15·1 volts. From the quantum relation $eV = hn$ we can calculate the frequency n corresponding to the ionising velocity V, which should be the maximum frequency obtainable from argon for this type of ionisation. Taking $e = 4{\cdot}77 \times 10^{-10}$ E.S. units and $h = 6{\cdot}55 \times 10^{-27}$ grm.cm.^{2}/sec., we obtain the value $3{\cdot}67 \times 10^{15}$ as the limiting frequency in the spectrum of argon. This corresponds to a wave-length of 817 Å.U. The extreme ultra-violet spectrum of argon has recently been investigated by Lyman,† who has found that the spectrum terminates abruptly near λ 800, so that the value we have found for the minimum ionisation velocity confirms the spectroscopic evidence.

Although an electron moving with a velocity acquired by falling through a potential difference of 15·1 volts is able to ionise an argon atom on colliding with it, such collisions do not always result in ionisation. A certain amount of evidence has been obtained that, when the electron velocity is greater than the critical ionising value, the fraction of the total number of collisions which result in ionisation is greatly increased by the presence of intense 11·5 volt radiation, for, as has already been pointed out in connection with the big increase of positive current shown at 18·1 volts in fig. 8, a large increase in the radiation led to an abrupt and very large increase in the ionisation, although no alteration was made in the external conditions. This result suggests that some ionisation may occur at electron velocities below 15·1 volts in the presence of sufficiently intense radiation. That no detectable amount of ionisation is produced below 15·1 volts, in the presence of such intensities of radiation as those to which the argon atoms were subjected in most of the experiments described in this paper, has been proved by special experiments to test for ionisation at the minimum radiation potential difference; and in the case of those experiments in which the argon atoms were exposed to much more intense radiation, and in which the current showed hysteresis in regard to the accelerating potential difference (such as the curves of fig. 8), no evidence of hysteresis below 15·1 volts was ever obtained, a fact which makes it appear unlikely that ionisation does occur below that velocity. Therefore it seems that, though the presence of intense radiation may affect the number of ionising collisions which occur, the minimum ionisation velocity is the same whether the radiation to which the argon atoms are exposed be weak or intense.

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* Sir J. J. Thomson, 'Phil. Mag.,' vol. 28, p. 620 (1914).

† T. Lyman, 'Astro.-phys. Jour.,' vol. 43, p. 89 (1916).

An Investigation of the Effects of Electron Collisions with Platinum and with Hydrogen, to ascertain whether the Production of Ionisation from Platinum is due to Occluded Hydrogen.

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(Communicated by C. T. R. Wilson, F.R.S. Received December 10, 1919.)

In the course of an investigation of the effects of electron collisions with helium atoms,[*] it was found that positive ions were produced from a positively charged platinum gauze when this was bombarded by electrons with a minimum velocity of about 11 volts. The production of positive ions in this way does not appear to have been observed before for such small velocities of the impacting electrons, though their detection with primary rays of 30 volts speed is recorded by Campbell in the account of his experiments on ionisation by charged particles.* In this paper Campbell gives an excellent summary of the work which has been done in connection with the bombardment of metal surfaces by slow cathode rays. The work of Lenard, Baeyer, Gehrts, Campbell, and others has established the facts that, when such rays fall on a negatively charged metal surface, electrons leave the surface, and that the number and the speed of these electrons depends on the velocity of impact of the primary stream. When the velocity of the incident rays is less than 11 volts, the electrons leaving the plate are those of the primary stream which have been reflected at the metal surface, the characteristic of these reflected rays being that most of them have a velocity comparable with that of the incident rays. When the velocity of impact reaches 11 volts, in addition to reflexion, an excitation of secondary rays begins and gradually increases in amount as the speed is further increased up to about 200 volts. On this account the curve showing the relation between the velocity of impact and the number of electrons leaving the plate takes an upward turn at 11 volts, but no other bend occurs until 200 volts is reached. It has therefore been concluded that the two processes mentioned above, viz., reflexion, and excitation of secondary rays beginning at 11 volts, are the only causes of electrons leaving the impacted surface. It was found by Baeyer† that with a minimum velocity of impact of about 25 volts more electrons leave the plate than fall on it, and this result, combined with the fact that Campbell detected a positive current (presumably from a positively charged plate) when the bombarding electrons had a minimum velocity of 30 volts, has given rise to the view that the second process—that which is operative above 11 volts—is an ionisation at the metal surface, the material ionised being either the metal itself or gas attached to it. On this view it is concluded that the critical velocity of 11 volts is the "ionisation potential" of the material ionised. This velocity was found to be the same for all the metal surfaces tested, and as it agreed with the usually accepted value of the "ionisation potential" for hydrogen, it has been suggested that the material ionised is hydrogen present in the surface of the metal. Some confirmation of this view has been obtained by Campbell from experiments with metal surfaces subjected to treatment designed to modify the amount of hydrogen present,‡ but the evidence hitherto produced cannot be said to prove conclusively that the process which begins at 11 volts is a genuine ionisation by electron collisions. That ionisation occurs ultimately can hardly be doubted, for it has been observed that when the velocity of the electron stream is sufficiently increased, the number of electrons leaving a bombarded electrode is in some cases as much as twenty times as great as the number arriving at it,* but the first direct proof that ionisation occurs at the metal surface when the impacting electrons have a velocity as small as 11 volts seems to be that given by the experiments made in the course of our investigation of the ionisation of helium.

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[*] 'Roy. Soc. Proc.,' A, vol. 95, p. 408 (1919).

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* N. R. Campbell, 'Phil. Mag.,' vol. 25, p. 803 (1913).

† O. v. Baeyer, 'Phys. Zeit.,' vol. 10, p. 176 (1909).

‡ N. R. Campbell, 'Phil. Mag.,' vol. 28, p. 286 (1914).

The present research is a fuller investigation of this effect, undertaken in order to ascertain whether the evidence of ionisation at 11 volts could be substantiated, and, if so, to determine whether it should be attributed to the metal itself or to hydrogen attached to the metal surface.

Description of the Apparatus.

The apparatus used in these experiments is shown diagrammatically in fig. 1. The source of electrons is a short piece of tungsten filament, D, which can be heated to incandescence by means of an electric current. The apparatus was placed so that the temperature of the filament could be ascertained by means of an optical pyrometer.† C is a platinum thimble, the top of which is plane and about 2 mm. above the filament. The electrons from D are driven towards C by a difference of potential, V_1 volts, applied between the negative lead of the filament and C. The electrons from a small area at the middle of the filament pass through a circular hole in the centre of the top of C, directly over the filament. The electrode B, 4 mm. above C, consists of a plane circular piece of fine platinum gauze, about 2 cm. in diameter, which forms the base of a hollow cylinder of platinum foil, in which a circular platinum plate, A, 1 cm. in diameter, is fixed about 2 mm. above the gauze and parallel to it. The metal parts of the apparatus shown in the figure are enclosed in a glass containing vessel, which is connected to a mercury vapour pump and a McLeod gauge through a U-tube, which, during the experiments, was kept cooled in either liquid air or solid carbonic

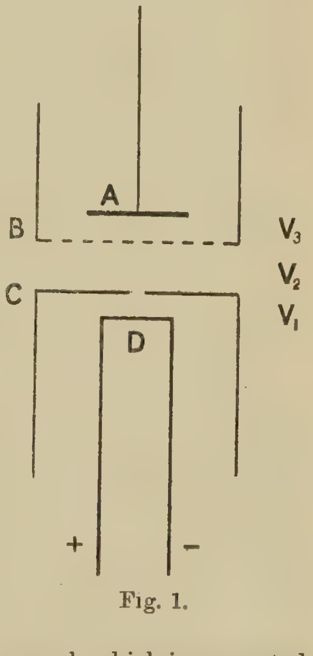

Fig. 1.

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* A. W. Hull, 'Proc. Inst. Rad. Eng.,' February, 1918.

† I am indebted to the Government Grant Committee of the Royal Society for the means of purchasing this instrument.—F. H.

acid, so as to prevent mercury vapour from entering the essential part of the apparatus. This was shut off by a stopcock from the mercury vapour when the apparatus was not in use. In order to prevent the electron stream, passing through the hole in C, from spreading laterally, a magnetic field parallel to the axis of the tube was applied by passing an electric current of 2 ampères through a coil of many turns of wire wrapped round the tube. The form of the electrodes B and C prevents any electrons from D from reaching A without traversing each of the fields between consecutive electrodes. The potential difference applied between C and B will be referred to as V_2, that between B and A as V_3. The currents to the collecting electrode, A, were measured by a sensitive Dolezalek electrometer in connection with it.

All the platinum used in the apparatus was boiled for many hours in strong nitric acid before being fitted into position, and the whole apparatus was finally washed out with chromic acid, followed by distilled water, in order to remove traces of grease from handling. The long-continued boiling of the platinum with nitric acid tends to remove hydrogen from its surface. The removal of hydrogen was rendered more complete by baking the experimental tube at a temperature of about 300° C. after it had been fitted into position and evacuated as completely as possible. During the process of baking, the tungsten filament was maintained at a white heat by an electric current and the apparatus was pumped continuously, except during the intervals when the rate of evolution of gas was being tested. The process was continued for several days until the evolution of gas had practically ceased.

Experiments in which the Collecting Electrode was Bombarded by the Electron Stream from the Filament.

In these experiments, the potential difference V_1 between the filament and the electrode C was maintained constant, and the speed of the electrons was varied by gradually varying one of the fields, V_2 or V_3, while the other remained constant. The direction of the field V_2 was always such as to drive electrons towards the collecting electrode. In some experiments the final field V_3 further accelerated the electrons, so that the velocity with which they impinged on the plate A corresponded to an applied potential difference of $(V_1+V_2+V_3)$ volts. In other cases the direction of V_3 was reversed, so that the electrons made "uphill collisions," striking the plate with a velocity corresponding to $(V_1+V_2-V_3)$ volts. In every case a correction has to be added to the total applied potential difference, in order to obtain the velocity of the swiftest electrons present under the particular conditions of experiment. This correction varied from 0·9 volt to 2·9 volts.

The current measured in these experiments is the difference between that due to the cathode rays which reach the plate A and that carried by the electrons which leave it. It was found that when all the fields were accelerating the electron stream, the current measured by the electrometer increased at first with increasing potential difference, but ultimately reached a value which varied very little for further increases of impacting velocity up to about 60 volts. Such change as was detectable over this range showed that the measured current increased a very little with increase of the velocity of the electrons. The value of the impacting velocity at which this almost constant current was first obtained varied slightly according to the distribution of the total accelerating potential difference between the fields V_1, V_2, and V_3, but was never more than about 10 volts. In cases where V_3 was kept at a constant value of 2 or 3 volts, and the speed of the electrons was varied by gradually increasing the potential difference V_2, the approximation to constancy of the current was less complete than when the field V_2 was kept constant and V_3 varied. This is readily explained on the view, already established by the work of other experimenters, that electrons are reflected at a metal plate with a velocity comparable with that of the impacting electrons for values of this velocity up to 11 volts, and that the amount of reflection occurring decreases as the velocity of impact increases. In the case where V_3 is small, the reflected electrons will be able to get away from the plate even though the direction of the field opposes them, whereas in the case where the speed of the electrons is altered by gradually increasing V_3, the reflected electrons will experience more and more difficulty in getting away from the plate as V_3 is increased, and will ultimately be prevented from escaping. Thus when V_3 is the varying field, a stage will be reached when no reflection can occur and the measured current corresponds to the total number of electrons from the filament which reach the plate.

When the field V_3 opposed the electrons from the filament and caused them to make "uphill collisions" with the collecting electrode, it was found that the measured current increased rapidly with the accelerating potential difference, until the velocity of impact was about 3 volts, but that when this value had been reached, the current either immediately decreased with increasing velocity of the impinging cathode rays, or increased at a much less rapid rate, finally reaching a stage when it did decrease with increasing electron speed. In every case the measured current had begun to decrease with increasing electron speed when the applied accelerating potential difference was between 10 and 11 volts. The same result was obtained whether the velocity of impact was varied by keeping the field V_3 constant and gradually increasing the accelerating potential difference V_2, or whether it was varied by keeping V_2 constant and gradually altering the magnitude of the potential difference V_3 retarding the primary electrons. The variations in the measured current were investigated for velocities of impact up to 70 volts, and in every case so long as V_3 opposed the electrons from the filament, and was greater than about 5 volts, the decrease of measured current with increasing electron speed continued over the whole range investigated.

Fig. 2 serves to illustrate the effects produced in the two cases we have considered, namely, when the electrons make "uphill collisions," and when they fall on a positively charged plate. The fields V_1 and V_2, accelerating the electron stream, were constant, and had a combined value of 27·0 volts. The speed with which the electrons struck the plate A was varied by varying the potential difference V_3. Observations of the current to the plate were taken for a range of values of V_3, extending from a negative value large enough to prevent any of the electrons from the filament reaching the

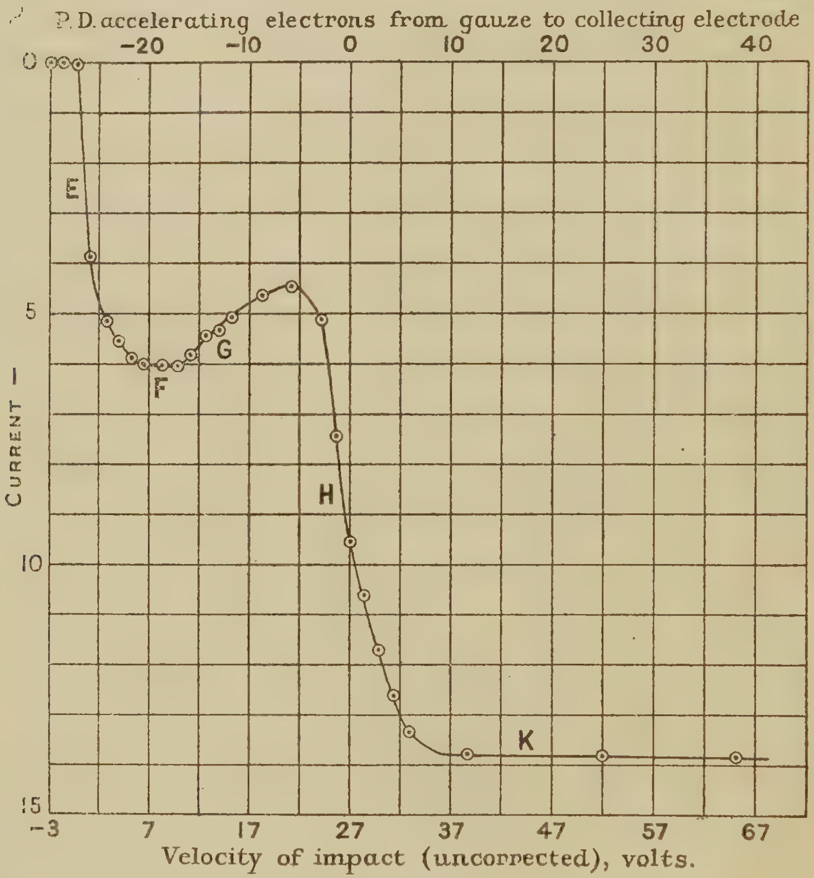

Fig. 2.

plate A, to a positive value of about 40 volts. Thus, as the velocity of impact increases, the final field, V_3, is reversed at a certain stage. The velocity of impact corresponding to any value of the field V_3 can be seen by reference to the lower horizontal scale in the figure. The curve shows first a stage where no electrons reach the collecting electrode, then, E, a rapidly increasing negative current due to the original electrons getting through to the plate, and, after this, a stage, F, where the current increases less rapidly, and attains an almost constant value. This latter part of the curve can be explained by the occurrence of reflexion of the impacting electrons, which prevents the measurement by the electrometer of the total number of electrons from the filament which reach the plate. This is followed by a fourth stage, G, where the current decreases as the velocity of impact increases, indicating that excitation of secondary rays is occurring, and becoming of gradually increasing importance. This stage begins when the velocity of impact of the electrons, as read from the lower horizontal scale in fig. 2, is between 10 and 11 volts, thus showing that the excitation of secondary rays requires a minimum applied potential difference between these limits. From the curve, it may be seen that the stage G continues until the potential difference V_3, retarding the electron stream, becomes less than about 5 volts, after which it is succeeded by a stage, H, where the negative current increases rapidly as the velocity of impact is increased further. The sharp downward bend in the curve between the parts G and H indicates that the number of electrons leaving the collecting electrode begins to decrease at this stage, thus causing the resultant negative current to the plate to increase rapidly as the direction of the field V_3 changes sign. This increase of current continues until the potential difference *opposing* the escape of electrons from the plate is increased to about 9 volts, after which the curve shows a stage, K, where the current remains approximately constant, increasing only a very little for a considerable increase in the velocity of impact. This constant value of the current may be taken as a measure of the current carried by the impacting electrons, and, since it is first attained when V_3 has a positive value of 9 volts, the maximum velocity of electrons leaving the plate is equivalent to that acquired by a fall through a potential difference of this amount. This value of the maximum velocity of the secondary rays is about the same as the value found by Lenard and by other observers. From the part K of the curve, it may be concluded that, if ionisation occurs at the metal surface, the number of positive ions which leave the plate A (now positively charged with respect to the gauze B) must be small compared with the number of electrons reaching it from the filament. On the other hand, it may be seen from the relative magnitudes of the currents in the parts G and K of the curve, that when the plate is negatively charged with respect to the gauze B, the number of electrons which leave the plate is comparable with the number which reach it from the filament. This difference is to be expected, since any positive ions, produced by ionisation, will escape from the surface less readily than electrons. In seeking evidence of ionisation at the bombarded surface, such as would be afforded by the detection of positive ions leaving the surface, it is clearly desirable to arrange the experiment so that any current due to positive ions is not superposed upon the large current due to the electron emission from the filament, but is investigated independently. Experiments for this purpose are described in the next section of this paper.

Experiments to Test for the Liberation of Positive Ions at the Minimum Electron Velocity at which the Production of Secondary Rays Begins.

In the preceding section, it has been pointed out that, in seeking evidence of the production of positive ions at the metal surface as a means of ascertaining whether ionisation by electron collisions occurs, a sensitive test can only be made if the electron stream from the filament is prevented from reaching the collecting electrode. This condition was secured by arranging the electric fields so as to turn the stream back to bombard the upper surface of one of the electrodes B or C (fig. 3). In the earlier experiments, the electrons from the filament were accelerated up to the electrode C by a constant potential difference, V_1, and were further accelerated by a variable potential difference, V_2, applied between the electrodes C and B. A constant difference of potential was maintained between the gauze B and the plate A. This opposed the electron stream, and was large enough to prevent any of the electrons from the filament from reaching the plate, even for the highest values of V_2 employed. The cathode rays thus bombarded the upper surface of the gauze B, which was charged positively with respect to the plate A. Since the potential difference V_3 is in all cases greater than (V_1+V_2), no electrons reflected from B could possibly reach A, and the electrometer

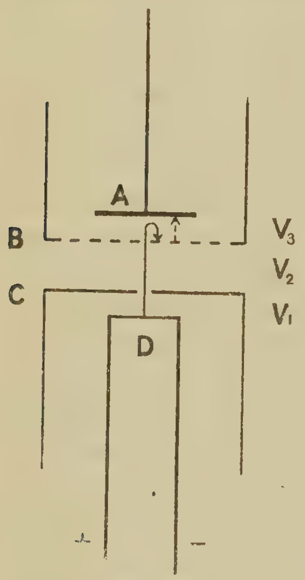

Fig. 3.
Path of electrons represented thus ⟶.
Path of positive ions represented thus - - - ->.

should not indicate a current until some effect, other than reflexion of the cathode rays, occurs at the bombarded surface. It was found that the electrometer measured a positive current, beginning when (V_1+V_2) was about 11 volts, and increasing rapidly as this potential difference was further increased. It is possible to account for this current in two ways :—

1. As being due to the collection of positive ions produced by ionisation at the surface of the electrode B by the bombardment of the cathode rays.

2. As being due to the liberation of electrons from the collecting electrode by the photo-electric action of a radiation produced by the impacts of the cathode rays on the surface of B.

In order to discriminate between these two possible explanations, experiments were made in which the electric fields were arranged so that the electron stream bombarded the upper surface of the electrode C, with a velocity which could be varied by varying V_1, and the field V_3 was such that positive ions liberated from the bombarded electrode C would cause the electrometer to indicate a positive current, while the photo-electric action of a radiation produced by electron impacts would tend to cause the electrometer to indicate a negative current. This arrangement was secured by making the potential difference V_3 small (about 3 volts), and opposite in direction to V_2, so that positive ions liberated from the electrode C, and driven towards the gauze B by the large field opposing the electron stream, would still be able to reach A. The small potential difference V_3 enables any photo-electrically active radiation produced to liberate electrons from the upper surface of the gauze B, and thus cause a deflexion of the electrometer in the opposite direction to that given by positive ions. Fig. 4 is a typical example of the curves showing the variation of the measured current with increasing accelerating potential difference obtained under these conditions. It may be seen that a positive current is measured, beginning when the applied accelerating potential difference V_1 has a value between 10 and 11 volts, and increasing rapidly with increasing values of the velocity of impact. This experiment therefore proves that, when the electrons emitted by the glowing filament fall through a potential difference of 10 or 11 volts, some of them are able to produce ionisation at the surface of the platinum plate. The actual velocity with which electrons bombard the plate in the experiment is greater than that corresponding to the applied potential difference, on account of the velocity with which they are emitted from the filament, but a correction to the applied potential difference to allow for this does not seem to have been always made by other investigators.

The potential difference mentioned above is about that which has been found by Franck and Hertz and by other experimenters to be the potential difference through which an electron must fall in order to produce ionisation in hydrogen. Recently, Davis and Goucher* have investigated the ionisation of hydrogen more fully by a method capable of discriminating between ionisation and the photo-electric effects of a radiation, and have concluded from their results that, at a minimum electron velocity of 11 volts, both ionisation and radiation are produced. They also claim to have detected the production of a second type of radiation at 13·6 volts and a second type of ionisation at 15·8 volts. Their results regarding the occurrence of two types of ionisation are in agreement with the experiments of Bishop.†

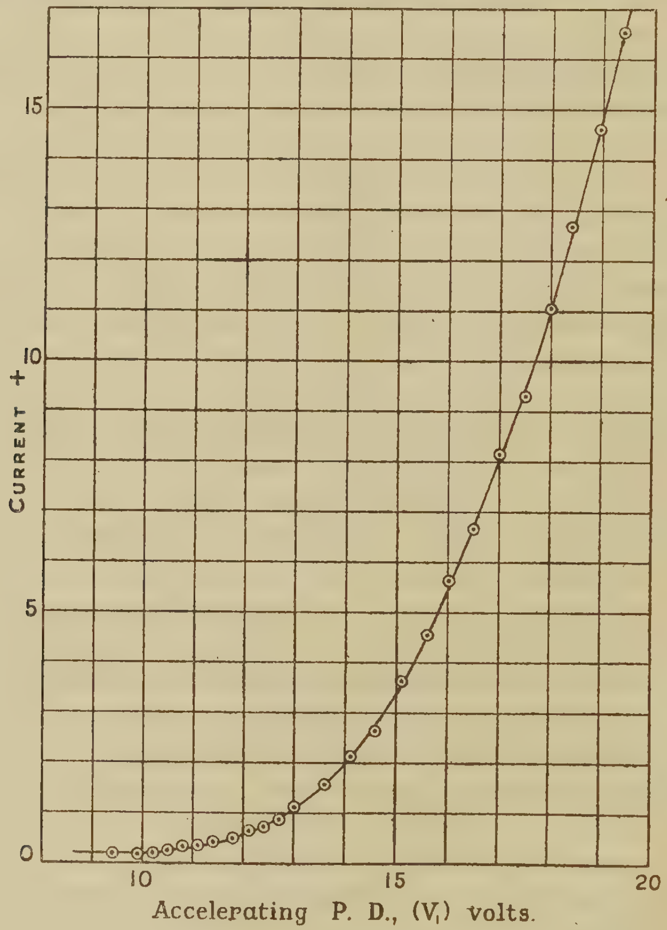

Fig. 4.

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* B. Davis and F. S. Goucher, 'Phys. Rev.,' vol. 10, p. 101 (1917).

† F. M. Bishop, 'Phys. Rev.,' vol. 10, p. 244 (1917).

It has been mentioned earlier that the fact that the excitation of secondary rays from an impacted metal plate begins when the electrons fall through an applied potential difference of between 10 and 11 volts, led to the suggestion that the rays were produced by ionisation of hydrogen attached to the metal surface. The proof that a genuine ionisation by electron impacts occurs at this point is given by the experiments described at the beginning of this section. Conclusive evidence that the material ionised is hydrogen would be available if it could be established that ionisation of hydrogen begins at precisely the same electron velocity as the ionisation at the impacted surface, and that all the other effects found to occur with hydrogen occur also at the same critical velocities when the electrodes are bombarded in the absence of gas. On the other hand, the absence, in the case of the bombarded platinum, of some of the effects observed in hydrogen would not necessarily disprove the suggestion that it is this gas which is being ionised at the platinum surface, since hydrogen under normal conditions is in the molecular state, while such evidence as is available as to the condition of hydrogen contaminating a metal surface points to its being in the atomic state.*

In attempting to establish the identity of the material ionised, the critical electron velocity at which ionisation could first be detected was carefully investigated for different temperatures of the filament. Every determination of the minimum applied potential difference at which positive ions could be detected was followed immediately by an estimation of the correction to be applied to give the velocity of the swiftest electrons present when this potential difference was applied from the cells. Assuming that the swiftest electrons which bombard the platinum surface are numerous enough to produce a measurable amount of ionisation, this critical value gives the minimum electron velocity at which the effect occurs. In the accurate determinations of the critical velocity for the production of ionisation at the bombarded surface, the uncorrected values obtained directly from the current-potential difference curves were in all cases between 10 and 11 volts. In obtaining the correction, the directions of the fields were the same as in the actual experiments for the detection of ionisation, and as in these experiments, V_1 was the only varying field. The potential difference V_2 opposing the electron stream was maintained at some constant value, smaller than the value of the applied potential difference at which ionisation was first detected. The potential difference V_3, which was such as to drive electrons towards the collecting electrode, was 3 volts in most of the experiments for determining the correction. This ensured the collection of any electrons from the filament which succeeded in reaching the gauze B against the opposing potential difference V_2, and which passed through this gauze. The difference between the values of V_1 and V_2 when a current was first detected gave the correction to be added to the potential difference V_1 to give the velocity of the swiftest electrons present. This was found to have a positive value ranging from 2·5 volts to 2·9 volts under different conditions. The mean of all the corrected values gave 13·0 volts as the critical electron velocity for the production of ionisation. It appears from this result that the ionisation produced when slow cathode rays fall upon a platinum plate requires a minimum electron velocity which does not agree with the usually accepted value of the "ionisation potential" of hydrogen (11 volts). We next tested to see whether a sudden increase of ionisation occurred anywhere in the neighbourhood of 15·8 volts, but no sign of a sudden bend in the current curve could be detected. The continuous increase of current which was measured over a range extending up to 20 volts is well illustrated by the curve of fig. 4, which is typical of the results obtained in these experiments.

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* O. W. Richardson, J. Nicol, and T. Parnell, 'Phil. Mag.,' vol. 8, p. 1 (1904).

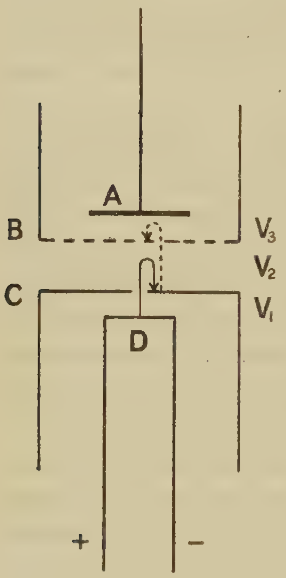

Fig. 5.
Path of electrons represented thus ⟶.
Path of positive ions represented thus - - - ->.

In testing for the production of a radiation, the electric field V_3 was increased to 35 volts so as to prevent the positive ions from reaching the collecting electrode. Under these conditions, the electrometer should indicate no current unless the electron impacts on the metal surface give rise to a radiation capable of acting photo-electrically on the metal, or until the impacts of the positive ions, which are turned back to bombard the upper surface of the gauze B, fig. 5, cause electrons to leave that surface.* On testing, it was found that the electrometer gave no indication of any current even when the electron velocity had been raised to 30 volts. Thus no detectable amount of photo-electrically active radiation is produced by the impact of electrons on a platinum surface with velocities up to this value. According to Bohr's theory it would appear to be always possible to produce radiation from electron impacts with atoms for lower electron velocities than those necessary to produce ionisation, since the latter corresponds to the complete removal of an electron from the atom, while in the former case the electron merely suffers a displacement within the atom. In many of the experiments that have been made with metallic vapours, and in some of the experiments with gases, radiation has been detected at lower electron velocities than ionisation. It might, therefore, be expected that since cathode rays falling upon platinum produce ionisation at 13 volts, they would give rise to radiation at some smaller velocity of impact. That such a radiation can be produced from metal plates when bombarded by slow cathode rays has been demonstrated by Sir J. J. Thomson, who, by the use of a photographic method, has recently detected the production of radiation by electrons with velocities as low as 10 volts.* The detection, in the present experiments, of radiation from the platinum atoms would depend upon the power of this radiation to act photo-electrically on a surface of the same metal as that from which it would be produced. It is, moreover, to be observed that the relative magnitudes of the currents due to radiation and to ionisation in a case where both are produced must depend upon the characteristics of the apparatus employed to detect them. Before concluding from the absence of radiation that the ionisation at 13 volts is not due to hydrogen, it was therefore necessary to ascertain whether, with the form of apparatus used in these experiments, the radiation produced in hydrogen was easily measurable when the ionisation was of the magnitude of that taking place at the platinum surface.

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* 'Roy. Soc. Proc.,' vol. 95, A, p. 333 (1919).

An Investigation of the Production of Radiation and Ionisation by Electron Collisions in Hydrogen.

The hydrogen used in these experiments was allowed to diffuse into the apparatus through a palladium tube heated in a Bunsen flame. The pressures used varied in different experiments from 0·015 mm. to 0·45 mm. The methods of experiment were those used in testing for ionisation and radiation in the experiments already described, and the range of filament temperatures was about the same as before. On account of the limitations imposed by the form of the present apparatus (which was not designed for the investigation of the effects of electron collisions with gases) the critical electron velocities for hydrogen could not be detected with the same degree of certainty as would have been possible with the apparatus used in our experiments with helium and argon, but there can be no doubt that the results obtained give a general indication of the effects which occur.

The investigation of the production of radiation in hydrogen was carried out at various pressures and a radiation was first detected when the velocity of the electron stream reached about 10·5 volts. Many of the radiation curves obtained showed a distinct bend indicating the occurrence of a new type of radiation at an electron velocity of about 13·9 volts. Both the critical voltages mentioned are the values obtained by adding to the potential difference applied from the battery, a correction determined experimentally in the manner described in the last section. The magnitude of the radiation currents produced by collisions of the 10·5 volt type was small compared with the magnitude of the radiation currents resulting from the second type of radiating collision. In some instances it escaped detection altogether, but careful investigations at pressures of about 0·02 mm. to 0·07 mm. leave no doubt as to the production of radiation at 10·5 volts. Fig. 6 is a typical example of the radiation curves obtained at low pressures. This shows radiation of the first type beginning when the applied potential difference is 7·8 volts and radiation of the second type beginning when the applied potential difference is 11·3 volts.

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* Sir J. J. Thomson, 'Phil. Mag.,' vol. 28, p. 620 (1914).

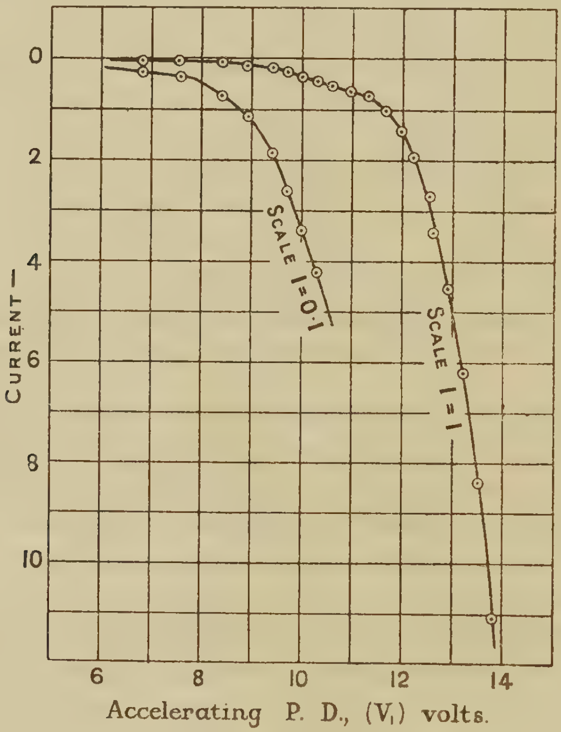

Fig. 6.

The production of ionisation in hydrogen was investigated by two methods. In one of these the direction of the field V_3 was arranged so as to cause radiation to give a current in the opposite direction to that due to ionisation.

In the other method the effects of radiation were eliminated as far as possible by making V_3 zero. In the experiments by the latter method, a positive current (showing the occurrence of ionisation) was first detected when the electron velocity was about 13 volts and distinct bends in the current-potential difference curve were obtained at values of the applied potential difference corresponding to electron velocities of about 14·4 volts and 16·9 volts respectively. These are the mean corrected values found from several experiments. The uncorrected values of the potential difference at which these points occurred in a typical case, may be seen by reference to fig. 7, which gives the results of a series of observations in hydrogen at a pressure of 0·073 mm. with the filament at a temperature of 1400° C. In investigating the production of ionisation in hydrogen by this method it must be borne in mind that the photo-electric effect of the radiation produced in the gas may not be completely eliminated by making V_3 zero, for it is probable that the radiation falls unequally on the collecting electrode, and on the surrounding cylinder and gauze B. On account of the velocity of emission of the photo-electrons, the electrode which receives more radiation will gain a positive charge, and thus, when radiation is produced from the gas, there may be a resultant photo-electric current in the same direction as a current due to ionisation, so that a bend in curves like those of fig. 7 might possibly be due to radiation, and not, as we have stated above, to ionisation of the gas. Of the three critical velocities deduced from the curves of fig. 7, only that at

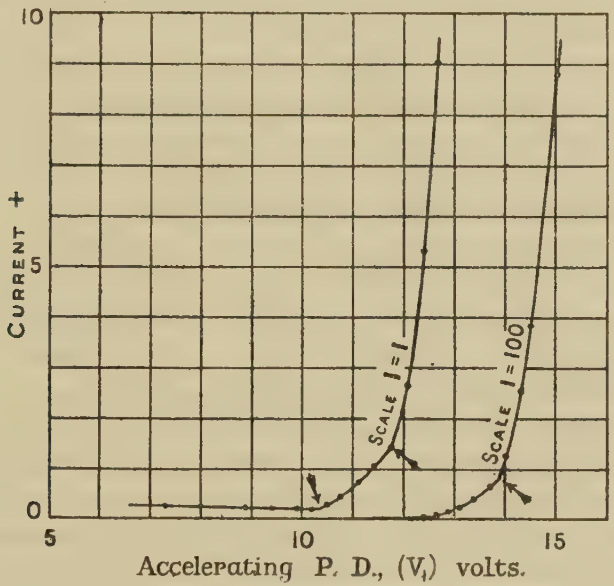

Fig. 7.

14·4 volts is sufficiently near to a critical velocity for radiation for it to be reasonable to suggest that it is due to the latter cause. That a second type of ionisation is really produced at this point was, however, shown by the tests made by the method in which a constant potential difference was maintained between the collecting electrode and the neighbouring gauze, so as to cause radiation to give an electrometer deflexion in the opposite direction to that given by the collection of positive ions. Observations by this method confirmed the existence of three critical velocities for ionisation at about the points indicated in fig. 7.

The first of the corrected values of the critical electron velocities found in these ionisation experiments is identical with the corrected value of the minimum electron velocity at which ionisation was detected when slow cathode rays bombarded platinum. This suggests that ionisation of the same material is occurring in both cases, and might at first be thought to provide evidence that the material ionised at the platinum surface is hydrogen, in which case 13·0 volts would be the "ionisation potential" of the hydrogen atom, and 14·4 volts and 16·9 volts would be assumed to correspond to ionisation of the hydrogen molecule. Arguments are advanced below to show that the ionisation detected at the first critical velocity, 13·0 volts, is not due to hydrogen, and it is concluded that the critical velocity 14·4 volts corresponds to the ionisation of the hydrogen atom and the critical velocity 16·9 volts corresponds to the ionisation of the hydrogen molecule. The following consideration shows that the ionisation produced by electrons with 13·0 volts velocity cannot be due to hydrogen. When ionisation occurs at a metal surface, it can only be produced from the layer of molecules or atoms just at the surface, but in the investigation of the ionisation of hydrogen the thickness of the layer of gas throughout which the electrons have sufficient velocity to cause ionisation increases continuously as the velocity of the electrons is increased beyond the critical value. It therefore follows that if 13·0 volts is the "ionisation potential" for hydrogen, the ionisation which has been found to begin at this voltage (irrespective of whether hydrogen is present or not) should increase at a more rapid rate when hydrogen is present than it does in a high vacuum. On the other hand, if hydrogen is not ionised until the electron velocity reaches 14·4 volts, we should expect the currents measured when the electron velocity is between 13·0 volts and 14·4 volts to be smaller when the apparatus contains hydrogen than when it is exhausted, because, in the former case, some of the electrons will lose energy by impact with hydrogen molecules, and so bombard the platinum surface with a smaller velocity than when no gas is present. An investigation of the rates of increase of the ionisation currents in the two cases was made by plotting together pairs of current-potential difference curves for which the filament temperatures were the same, one curve of each pair being a high vacuum curve and the other being for some definite pressure of hydrogen. Fig. 8 is a typical example of such a pair of curves; the dotted curve shows the currents obtained in the absence of gas and the continuous curve the currents obtained in hydrogen. It may be seen that both curves show a positive current which begins at an applied potential difference of 10·5 volts, but this current increases more slowly in the presence of hydrogen than it does in a high vacuum until the potential difference reaches the value 11·8 volts, after which the hydrogen curve shows the more rapid rate of current increase. From this it may be concluded that the hydrogen is not ionised until the applied potential difference V_1 reaches the value 11·8 volts, and that the ionisation which begins when V_1 is 10·5 volts is not due to hydrogen. The correction to be applied to these values was found to be 2·7 volts for both the curves given in fig. 8, so that the electron velocities corresponding to the critical potential differences are 13·2 volts and 14·5 volts respectively.

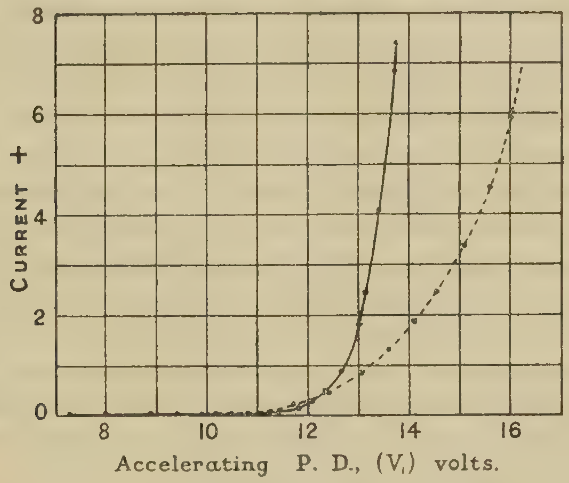

Fig. 8.

Further evidence that the ionisation which begins at 13 volts is not due to hydrogen, was obtained from experiments in which the currents due to ionisation and those due to radiation in this gas were measured independently under corresponding conditions. Experiments of this kind were made for a considerable range of hydrogen pressures and filament temperatures, and, with the exception of a few instances at the highest pressures, a current due to radiation of the first type (that which is produced by electrons with a velocity of 10·5 volts) was always detected. In every case the effects of radiation of the second type (13·9 volts) were observed. On the other hand, in the high vacuum experiments, no radiation of either type was ever detected. The radiation curve in fig. 6 and the continuous curve in fig. 8 (ionisation) afford an example of the relative magnitudes of the currents due to radiation and those due to ionisation in hydrogen, measured independently under corresponding conditions. Fig. 6 shows that radiation of the first type is easily measurable when the ionisation produced between applied potential differences of 10·5 volts and 11·8 volts is of the magnitude shown in the continuous curve of fig. 8. From the latter figure, it is clear that the ionisation current between these voltages is greater in the high vacuum experiment than in an atmosphere of hydrogen. We may assume that radiation of the first type is produced from atomic hydrogen, in which form the gas is known to exist when it is present in platinum. It follows, therefore, that the radiation current corresponding to an ionisation current of the magnitude shown in the dotted curve of fig. 8 should be easily measurable if this ionisation is produced from hydrogen. Thus, the fact that radiation is not detected in the high vacuum experiments is a proof that the effects observed are not due to hydrogen at the platinum surface.

Summary of Experimental Results.

The results of the experiments described in the foregoing pages are summarised below:—

1. The reflexion of slow moving cathode rays at a negatively-charged platinum surface for small velocities of the electron stream, and the excitation of secondary rays, with a maximum velocity of emission of about 10 volts, for higher velocities of the electron stream, have been verified, though no exact quantitative observations have been made.

2. It has been shown that the excitation of secondary rays is a genuine ionisation effect, and that it begins at a minimum electron velocity of 13·0 volts. No sign of the production of a radiation capable of acting photoelectrically on platinum was detected in the special experiments made to investigate this.

3. It has been proved by admitting hydrogen into the apparatus that the ionisation which begins at 13·0 volts is not due to hydrogen attached to the platinum surface, and is therefore probably produced from the metal itself.

4. The investigation of the effects of electron collisions with hydrogen has shown:—

α. That a radiation is produced at a minimum electron velocity of 10·5 volts.

β. That a second type of radiation is produced, beginning when the electron velocity reaches 13·9 volts.

γ. That ionisation of the gas occurs at a minimum electron velocity of 14·4 volts.

δ. That a second type of ionisation begins when the electron velocity reaches 16·9 volts.

A Discussion of the Results obtained with Hydrogen.

In view of the simple structure assumed for the hydrogen atom, the experimental investigation of the effects of electron collisions with this gas is of particular interest, since it provides a direct test of the validity of Bohr's theory. A comparison of the critical electron velocities obtained in this research with those deduced from Bohr's theory is given in the following table:—

	Critical electron velocities (volts).				
	Radiation from the atom.	Ionisation of the atom.	Radiation from the molecule.	Ionisation of the molecule.	Dissociation of the molecule.
Calculated from Bohr's theory ...	10·2	13·6	—	16·3	2·7
Determined experimentally	10·5	14·4	13·9	16·9	2·5

The theoretical value of the "ionisation potential" for the molecule is calculated on the view that the ionisation results in the production of an electron, a positive nucleus, and a neutral atom. The values obtained in this research for the first critical velocity at which radiation is produced, and for the two critical velocities at which ionisation is produced, are all rather higher than the calculated values. It has, however, been pointed out that the corrected values of the critical velocities are those of the swiftest electrons present when the effect is first detected, and the assumption has been made that the number of electrons with the maximum velocity is sufficient to give a detectable amount of radiation or ionisation. The velocity distribution curves obtained in these experiments showed that only a small percentage of the total number of electrons in the bombarding stream has the maximum velocity. It is therefore possible that, by deducing the correction from this maximum, the values obtained for the critical electron velocities are higher than those which actually produced the effect detected. This is particularly the case where the current due to the effect to be observed is superposed on a current due to an effect produced at a lower voltage. It therefore seems probable that the value determined for the first critical electron velocity (producing radiation at 10·5 volts) is likely to be more nearly correct than the values of the other critical electron velocities found for hydrogen. In the case of the radiation experiments, the current due to the second type of radiation has to be detected in the presence of the current due to the radiation of the first type. In the ionisation experiments, the current due to the ionisation of hydrogen atoms is superposed on the current due to ionisation at the platinum surface, and the current produced by the second type of ionisation has to be detected in the presence of both these ionisation currents. In this connection it is significant that all the experimental results are higher than the theoretical values, and that the agreement between the experimental and the theoretical values is closest in the case of the first critical velocity, which we have seen above probably approximates most nearly to the true value.

Since Bohr has shown that ionisation of the hydrogen molecule is most likely to involve the breaking up of the molecule into an electron, a positive ion, and a neutral atom, the difference between the "ionisation potential" of the hydrogen molecule and that of the hydrogen atom should give a measure of the energy required to dissociate the molecule into neutral atoms. The calculated and observed values of this difference are given in the last column of the table. It will be seen that, although the observed "ionisation potentials" are higher than those required by Bohr's theory, there is fairly good agreement between the theoretical and experimental values of the critical velocity for dissociation. This might perhaps be expected, since any error in the correction applied to the measured potential difference would probably be the same in the case of each "ionisation potential."

In hydrogen, under ordinary conditions, there are very few, if any, free atoms present, and if we are to assume, as we have done, that electron collisions with free hydrogen atoms take place in these experiments, the presence of these atoms must be accounted for. As far as the available evidence goes, it seems unlikely that much thermal dissociation of the gas takes place at the temperature of the filament, but an explanation of the presence of free hydrogen atoms is at once to hand if dissociation is produced by electron impacts at speeds of 2·5 volts or more. On this view it might perhaps be expected that a second radiation point would be detected corresponding to the stage at which the same electron collision could dissociate the molecule into atoms, and cause one of these atoms to emit radiation. The electron velocity at which this might be expected to occur in our experiments is 10·5 volts + 2·5 volts = 13·0 volts. It might perhaps be suggested that the radiation detected at 13·9 volts is produced in this way, but we are inclined to think that the discrepancy between the value 13·0 volts, deduced from the velocity at which the first type of radiation is produced and the experimentally determined value, 13·9 volts, at which the second type of radiation begins, is greater than could be accounted for by experimental errors. An alternative explanation of the production of the second type of radiation, detected at 13·9 volts in these experiments, is that it is produced from the hydrogen molecule as a result of the return of the electrons to their normal orbit after being displaced by the collision of an electron with a minimum velocity of this amount.

The results of Davis and Goucher's investigations with hydrogen have already been given. The critical velocities obtained by these investigators are not in very good agreement with those obtained in the present research, but the most important difference between their results and ours lies in the fact that they have concluded that at the first critical velocity (11 volts in their experiments) ionisation and radiation occur simultaneously. This involves an explanation based upon the splitting up of the *molecule* at this point, since radiation and ionisation cannot both be produced at the same minimum electron velocity from hydrogen atoms if their structure is the simple one usually assumed.

Bohr's theory of the structure of hydrogen atoms and molecules receives general support from the results of the experiments with hydrogen described in this paper, but it is desirable that the accuracy of the actual values of the critical velocities should be tested by experiments with an apparatus specially designed for this purpose.

Colloidal Electrolytes.—Soap Solutions and their Constitution.[*]

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I. *Introduction.*

Colloidal electrolytes are solutions of salts in which one ion has been replaced by a heavily hydrated polyvalent micelle, carrying an equivalent sum total of electrical charges and also serving as an excellent conductor of electricity. This is the conclusion to which our investigations have led us.

It will probably prove that this new class includes, under certain conditions, most organic compounds containing more than eight carbon atoms, and capable of forming ions, also solutions of the acid and alkali proteins, dyes, indicators, sulphonates, soaps, and possibly even of such compounds as chromium chloride, and of the alkaline tungstates, zincates, tellurates, and silicates. Many non-aqueous solutions may also be included in the same category, as will be shown in a later communication, and it is indeed probable that the class includes as many members as the acids and bases together.

II. *Résumé of previous Work.*

In 1905 one of us had shown that the available data with regard to solutions of such substances as cadmium iodide could be readily interpreted by means of the theory of ionic dissociation (without modifying it). In 1908 the investigation of solutions of salts, possessing simple formulæ, but exhibiting apparently abnormal properties, was extended to include the alkaline salts of the normal saturated fatty acids. In planning the investigation it was decided to adopt only such methods as had been employed in establishing the theories of solutions and of electrolytes, such as the measurement of freezing-points, of vapour-pressures, of electrical conductivities, etc. Viscosity measurements, and other methods employed in the investigation of colloids, were regarded as furnishing evidence of a circumstantial character only.

The first part of the investigation consisted in measuring the conductivities of solutions of sodium palmitate, over a wide range of concentration, near the boiling-point, at which alone they were liquid. The apparent boiling-points of numerous soap solutions had been measured by Krafft, but, as is shown in the present communication, the results arrived at, which had been accepted as a proof that soap was a simple colloid, were entirely erroneous.

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[*] Abridged manuscript.

The conductivity measurements proved conclusively that soap solutions possessed a high conductivity, not only when dilute, as had been shown by Kahlenburg and Schreiner, but even in the highest concentrations, indicating that soap solutions must consist of something other than neutral colloid. The next step was to show by two independent methods, namely, measurements of the rate of catalysis and of electromotive force, that the concentration of the hydroxyl ion in the solutions was negligible. *Hence the high conductivity must be due to the soap itself.*

III. *The Experimental Method.*

One of us, in conjunction with Miss Taylor, has already proved that neither the direct boiling-point method nor the tensimeter method can be used in the measurement of the vapour-pressures of soap solutions, owing to the impossibility of eliminating the errors due to the presence of air. For this reason, Krafft's observation that soap solutions boil at a temperature just above or just below the boiling-point of water, although perfectly correct, is entirely without significance. In the present investigation, therefore, the rise of boiling-point or lowering of the vapour-pressures of the solutions was measured by a modification of Cumming's *dew-point* method, in which the results are not influenced by the presence of air in the apparatus. This method made it possible to cover a wide range of concentration, from dilute solutions up to almost anhydrous solids. Independent measurements of a number of the solutions were made by each of us separately, and on subsequent comparison the maximum difference between our observations amounts to 0·01°.

Fig. 1 shows a diagram in vertical section of the apparatus employed. A highly polished silver tube, *a*, with silver bottom, is closed with a rubber stopper at the top. Through the stopper are inserted a thermometer and two tubes, through which a rapid current of water is circulated by a power pump from and to a thermostat of adjustable temperature. The silver tube is held in a cork in a glass vessel, which contains the solution to be studied. The top of the glass vessel rises an inch or so above the cork, so that the closed space is completely immersed in the water of a thermostat, which has glass slides. A capillary glass tube, sealed to a stopcock, passes through the cork holding the silver tube, and may be connected with a water pump and thus evacuated, or the pressure adjusted to any desired value.

The following procedure alone rendered possible the attainment of accurate results. Even if the silver tube is kept highly polished, it is extremely difficult to detect the first very slight dimming of the silver surface. This difficulty may, however, be overcome by treating a definite portion of the silver surface so that no dew deposits on it, and it therefore remains bright, directly contrasting with the slightly clouded surface adjacent to it. The test of the appearance, or disappearance, of dew is then by the first appearance of this sharp boundary or by the perfect uniformity of the surface. To produce this effect, boiling water is run through the silver tube, and the bottom angle at one side of the tube is dipped once into boiling conductivity water. The water evaporates at once, but thereafter no dew will form on that part of the surface which has been treated. When the tube is subsequently viewed from the front a boundary line runs diagonally across the lowest part of the side of the tube. An attempt was made to extend this refinement of the dew point method to various non-aqueous solutions, but without success, for in every case dew formed all over the silver surface.

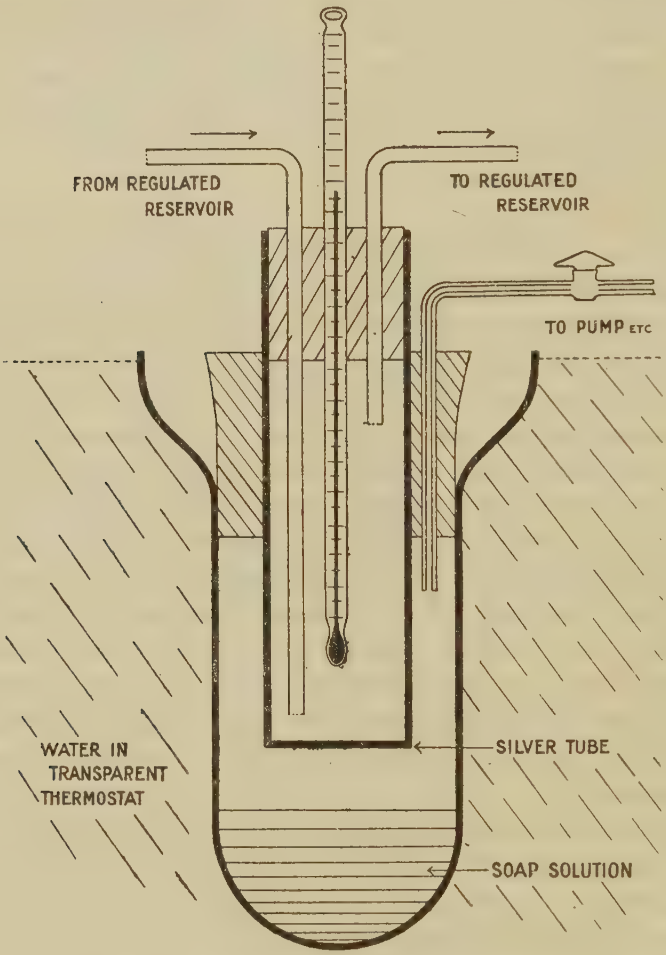
FROM REGULATED RESERVOIR
TO REGULATED RESERVOIR
TO PUMP ETC
WATER IN TRANSPARENT THERMOSTAT
SILVER TUBE
SOAP SOLUTION

Fig. 1.—Section of Dew Point Apparatus.

The transparent thermostat was connected with a constant level device and was filled with glycerine and water, the top being carefully covered to reduce evaporation. The liquid was stirred vigorously during an experiment. The sides of the thermostat were cleaned and polished. The auxiliary thermostat contained water under a layer of melted paraffin or was covered. It was heated by gas, controlled by screw-down valve with a divided head, so that the rate of heating could be rapidly and accurately adjusted.

In making an experiment, the temperature of the transparent thermostat was first adjusted, generally to 90°. Water, very near its boiling-point, was then circulated through the silver tube, which was inserted in the glass tube, so that the bottom of it was 1 cm. above the surface of the solution to be studied. The whole apparatus was then placed in the transparent thermostat, and so held that it was possible to shake it slightly, so as to renew the surface of the solution from time to time. After a few minutes, the stopcock sealed to the capillary tube was closed, but it was not found necessary to evacuate the air from the apparatus, as the small amount of air present caused no appreciable lag in the diffusion of the water vapour.

The temperature of the water running through the silver tube was now very gradually lowered, and on the first appearance of dew, shown by a slight discontinuity in the polished silver surface, the boundary line becoming faintly visible under bright and carefully adjusted illumination, both thermometers were read. The rate of the supply of heat to the auxiliary thermostat was then at once increased to a value which would cause the temperature of the running water to rise slowly. Though the dew at first increased, it soon became faint, and suddenly disappeared, the silver surface becoming sensibly uniform. The two thermometers were now read a second time. The temperature of the auxiliary thermostat was then again raised, and the whole cycle of operations repeated several times, so as to obtain a series of readings of the two thermometers at the points at which the dew formed and disappeared. The mean values for two series of seven or eight readings in either direction by independent observers show a negligible difference.

The results of a series of experiments are set down in Table I.

Measurements with two completely independent solutions on different occasions and involving eighteen readings gave as result 0·20° and 0·205°.

The difference between the temperature at which the dew forms and disappears is due to the alternate concentration and dilution of the surface layers of the soap solution, but it is probable that the error is equally distributed between the two sets of results, and that the mean of the two series gives the true dew point. In subsequent experiments, in which the solution was stirred, the difference practically disappeared. In determining the dew point with pure water, in order to arrive at the thermometer error and to eliminate personal error of observation, it was found that the difference never exceeded 0·03°.

Table I.—Dew Point of 1·0 N. Potassium Stearate at 90°.

Silver tube thermometer.	Thermostat thermometer.	Temperature difference.	
		Formation.	Disappearance.
89·43	90·00	(0·57)	
89·75	90·01		0·26
89·68	90·01	0·33	
89·75	90·00		0·25
89·68	90·00	0·32	
89·74	90·01		0·27
89·68	90·00	0·32	
89·75	90·01		0·26
89·69	90·00	0·31	
89·74	90·00		0·26
Mean		0·32	0·26
Final mean		−0·29°	
Thermometer error		−0·09°	
Rise of boiling point due to soap		0·20° at 90° C.	

IV. *The Method of Calculation.*

At the apparent dew point we have pure water, deposited on the silver tube, in equilibrium with its vapour, which is also in equilibrium with the soap solution, at a slightly higher temperature. The pressure of the aqueous vapour can be obtained by reference to standard tables, and the difference between the temperatures of the pure water and the soap solutions, as determined by the readings of the thermometers in the silver tube and in the transparent thermostat, corresponds to the rise of boiling-point of the solution, at that pressure, due to the presence of the soap. According to the familiar van't Hoff formula, $\Delta t = RT^2/\lambda$, the rise in boiling-point for a 1·0 N solution of crystalloid, such as sugar, at 90°, should be 0·483°, a value which is slightly lower than the value at 100°, as T is greater and λ is less at the higher than at the lower temperature. In calculating the results of measurements by the well-known Beckmann method at 100°, the rise of boiling-point is assumed to be 0·510°.

For lower temperatures, the values of the constant are: 70°, 0·414°; 45°, 0·353°; 25°, 0·303°; 20°, 0·291°.

The results calculated by the related formula, $ln(p/p') = n/\mathrm{N}$, give practically identical results, and it is worth emphasising the fact that these simple formulæ are still approximately correct even at high concentrations, the calculated osmotic effect always being higher than would have been anticipated. This is generally accounted for by assuming that the solute is hydrated. In a 2·7 N solution of cane-sugar, containing approximately equal weights of the constituents, the deviation is less than 12 per cent., and the hydrate appears to contain five molecules of water to one molecule of sugar.* These points have a certain bearing upon the results of the present investigation.

V. *The Experimental Results of the Dew Point Method.*

The solutions were prepared in silver tubes from Kahlbaum's best chemicals, employing all the precautions described in previous communications. The weight of palmitic acid required to neutralise a known amount of sodium hydroxide in aqueous alcohol was only 0·1 per cent. smaller than the theoretical amount.

Each concentration up to 1·5 N was prepared separately, and at least in duplicate. Concentrations are expressed invariably in weight normality (number of gram equivalent weights of soap in 1000 grams of water).

Almost every number in Table II and Table III is the resulting mean of several series of measurements, such as are given in Table I, carried out on independent solutions.

Table II.—Rise of Boiling Point at 90° for Potassium Salts.

Weight normality.	Stearate, C_{18}.	Palmitate, C_{16}.	Myristate, C_{14}.	Laurate, C_{12}.	Decoate caprate, C_{10}.	Octoate caprylate, C_8.	Hexoate caproate, C_6.	Acetate, C_2.
0·2 N	0°·10	0°·12	0°·13	0°·15	0°·16	0°·17	0°·17	0°·185
0·5 N	0·17	0·19	0·23	0·26	0·31	0·35	0·38	0·46
0·75 N	0·19	0·23	0·27	0·30	0·42	0·48	0·53	
1·0 N	0·20	0·24	0·28	0·32	0·52	0·60	0·66	0·86
1·5 N	0·16	0·21	0·25	0·31	(0·65)			
2·0 N	0·18	0·27	0·32	0·48	(0·72)	0·79		
3·0 N	0·23	—	—	1·02				

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* 'Trans. Faraday Soc.,' vol. 11, p. 39 (1915).

Table III.—Rise of Boiling Point at 90° for Sodium Salts.

Weight normality.	Behenate, C_{22}.	Stearate, C_{18}.	Palmitate, C_{16}.	Myristate, C_{14}.	Laurate, C_{12}.	Caprylate, C_8.	Acetate. C_2.	Any non-electrolyte by theory.
0·2 N	0°·09	0°·11	0°·13	0°·14	0°·15	0°·17	—°	0°·10
0·5 N	0·11	0·18	0·20	0·24	0·28	0·37	0·45	0·24
0·75 N	—	0·22	0·24	0·28	0·32	0·50	—	0·38
1·0 N	0·09	0·23	0·25	0·29	0·34	0·62	0·84	0·48
1·5 N	—	0·18	0·22	0·27	0·33	—	—	0·72
2·0 N	0·11	0·19	0·50	—	—	—	1·38	0·97
3·0 N	—	0·30	1·23	—	—	—	2·32	1·45

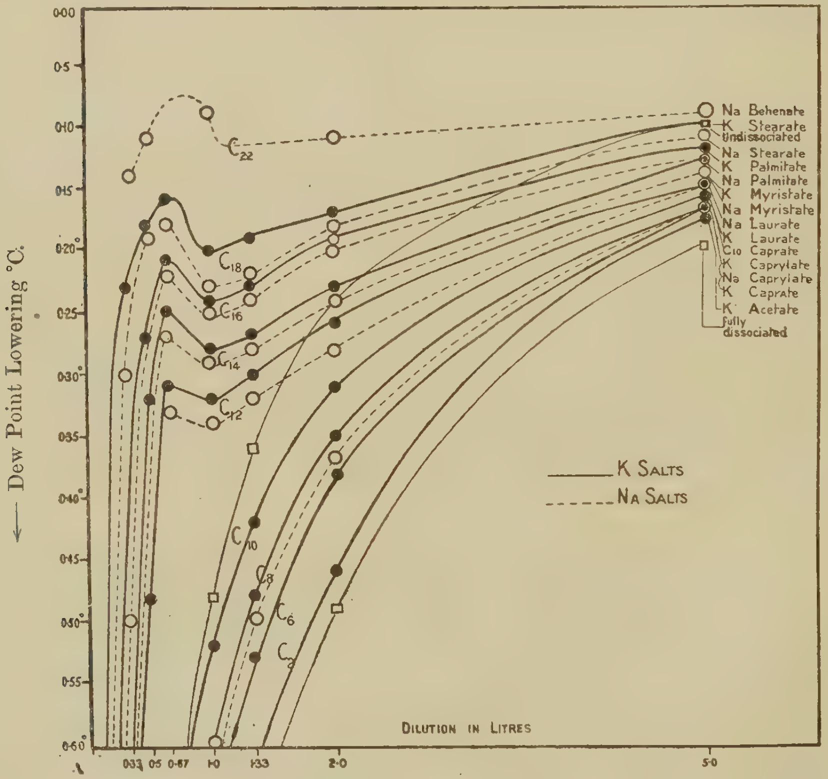

Fig. 2.—Dew Point Lowerings at 90° C. caused by Potassium and Sodium Salts of Fatty Acids.

Fig. 2 presents the directly observed dew point lowerings plotted against the dilution in litres as abscissæ. The curves for the sodium soaps are dotted in for convenience of comparison. It is evident that the salts fall into two classes. From the acetate up to the caprate (C_{10}) the curves are regular showing dissociation, although in the more concentrated caprate solutions the lowering only slightly exceeds that of an ordinary non-electrolyte. On the other hand, from the laurate (C_{12}) upwards, each curve passes through a pronounced maximum lowering at about 1·0 normal,* and a definite minimum lowering again at 1·5 normal. Above these concentrations the lowering rapidly increases again.

It is worth while remembering the physical properties of the solutions in question while discussing the regularity of the results. 1·5 N sodium stearate at 90° is a viscid gum. On the other hand, 2·0 N potassium laurate solution, with a similarly shaped curve, is a clear, oily liquid. The form of the curve is thus definitely due to the constituents in solution, not to mechanical effects, such as formation of gel or change of state. The effect is also not due to hysteresis, as is the case in the dehydration of certain gels, for it is independent of the age or method of preparation of soap solution, or whether water may have been previously added or taken away.

VI. *The Crystalloidal Constituents of Soap Solutions.*

Tables IV and V give the total concentrations of crystalloidal matter indicated by the data of Tables II and III, as shown in Section V above, and

Table IV.—Total Crystalloidal Matter in Potassium Salt Solutions at 90°.

Weight normality,	Stearate, C_{18}.	Palmitate, C_{16}.	Myristate, C_{14}.	Laurate, C_{12}.	Caprate, C_{10}.	Caprylate, C_8.	Caproate, C_6.	Acetate, C_2.
0·2 N	0·21	0·25	0. 27	0·31	0·33	0·35	0·35	0·38
0·5 N	0·35	0·39	0·48	0·54	0·64	0·72	0·79	0·95
0·75 N	0·39	0·48	0·56	0·62	0·87	0·99	1·10	
1·0 N	0·42	0·50	0·58	0·66	1·08	1·24	1·37	1·78
1·5 N	0·33	0·44	0·52	0·64	1·35			
2·0 N	0·37	0·56	0·66	0·99	1·50	1·64		
3·0 N	0·48	—	—	2·11				

Table V.—Total Crystalloidal Matter in Sodium Salt Solutions at 90°.

Weight normality.	Behenate, C_{22}.	Stearate, C_{18}.	Palmitate, C_{16}.	Myristate, C_{14}.	Laurate, C_{12}.	Caprylate, C_8.	Acetate, C_2.
0·2 N	0·19	0·23	0·27	0·29	0·33	0·35	
0·5 N	0·23	0·37	0·41	0·50	0·58	0·77	0·93
0·75 N	—	0·46	0·50	0·58	0·66	1·04	
1·0 N	0·19	0·48	0·52	0·60	0·70	1·28	1·74
1·5 N	—	0·37	0·46	0·56	0·68		
2·0 N	0·23	0·39	1·04	—	—	—	2·86
3·0 N	—	0·62	2·55	—	—	—	4·80

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* The exact concentration is slightly higher than 1·0 N for the lower members, and slightly lower than 1·0 N for the behenate. This agrees with the previous work on conductivity published from this laboratory, 'Trans. Chem. Soc.,' vol. 105, p. 435 (1914).

expressed in mols per 1000 grammes of water. This crystalloidal matter comprises K and Na; simple fatty acid ion, such as palmitate ion P; and simple undissociated neutral soap, such as sodium palmitate, NaP.

In fig. 3 the values of van't Hoff's factor "i," the ratio of the observed values of the lowering of the vapour pressures to the predicted values for solutions of any non-electrolyte of the same concentration, are plotted against the values of the dilution. The curves express the proportion of total crystalloids present, relative to that in the case of a non-electrolyte which is taken as unity, that of a completely dissociated binary electrolyte being 2.

It will be noted that the standpoint taken up differs from the crude treatment almost invariably accorded to measurements of "molecular weight" by the methods of ebullioscopy and cryoscopy, whether in aqueous or non-aqueous solution, where the data are simply scanned for evidence of association or dissociation. The usual interpretation is to conclude that, for example, a N/5 potassium stearate or a N/2 sodium myristate consists of simple undissociated molecules (a result which is, of course, irreconcilable with the conductivity, as in the case of many non-aqueous solutions). Similarly, a normal solution of sodium or potassium palmitate would be regarded as being composed of undissociated double molecules (again irreconcilable with the high conductivity). It will be seen how the method, developed under headings VI and VII, will probably clear up many otherwise unexplained anomalies in non-aqueous solutions, where such cases constantly occur.

The results cover a very wide range, from the ordinary highly dissociated electrolytes represented by the acetates to the concentrated solutions of the behenate (C_{22}), where the total amount of crystalloid, ionised and not, is only a tenth of the total concentration.

The regularity with which the phenomena set in is very striking, as we ascend the homologous series. The transition from any one type to the other is quite gradual. Again, the curves for each fatty acid run in pairs for the sodium and potassium salts. Only in concentrations above 1·5 N do the potassium and sodium soaps diverge appreciably, although in every case the potassium salt solution contains slightly more colloid. The last result had been already deduced from our study of conductivity.

VII. *The Combination of Osmotic with Conductivity Data.*

We have now the data derived from the experiments on vapour-pressure in suitable form to connect them with the data derived from conductivity experiments, with which they are at first sight at variance. The conductivity data which follow are based upon the values taken for the mobilities of the negative radicals at 90°: behenate to laurate 90, caprate 92, caprylate 94,

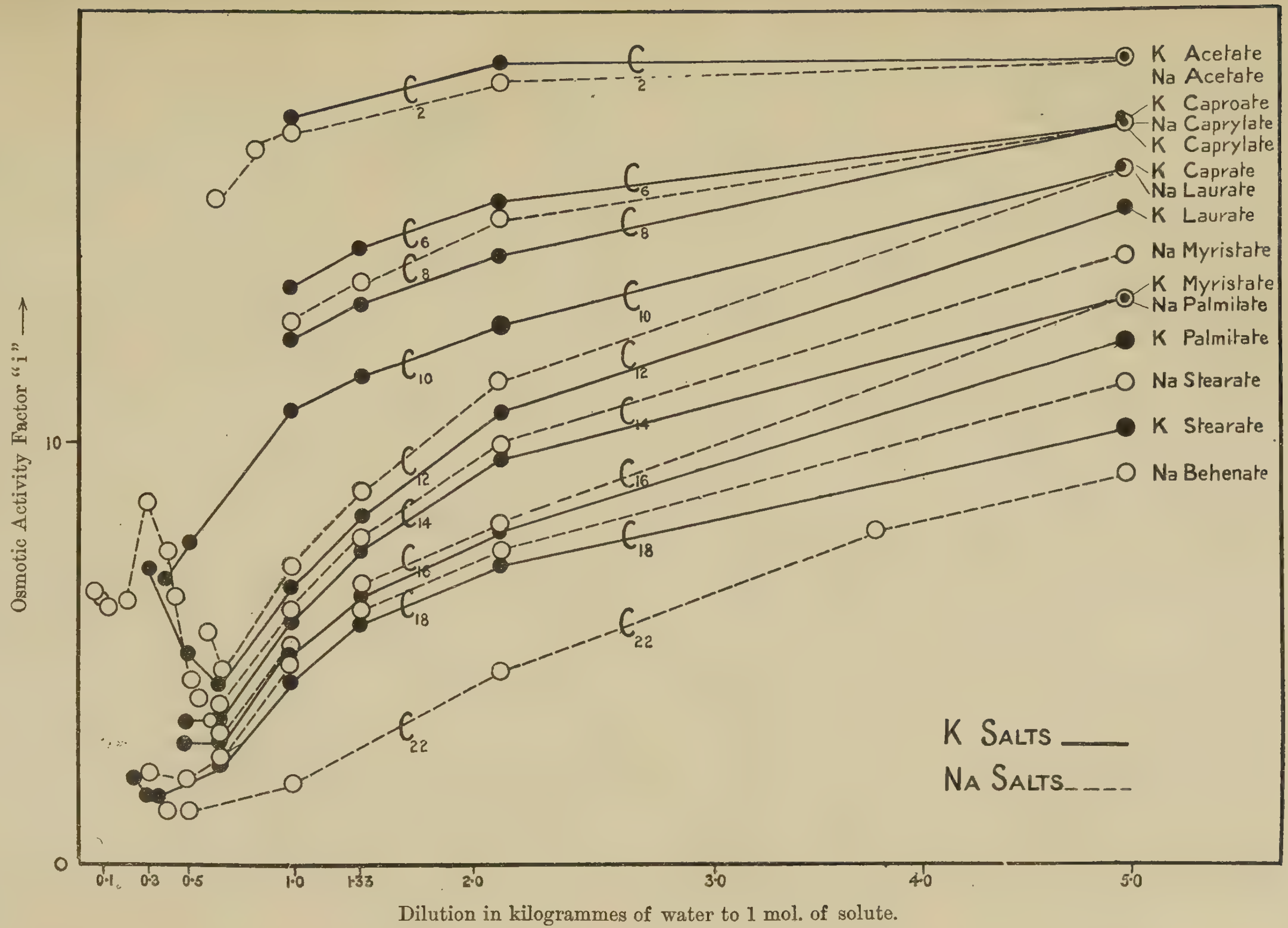

FIG. 3.—Relative Osmotic Activity. (10 in vertical scale should read 1·0.)

caproate 98, acetate 116, also sodium 139 and potassium 188. These are based partly upon the previous work,* partly on the measurements by A. A. Noyes and his co-workers at 100° for potassium and sodium chloride and acetate, and upon the extensive information which is available with regard to dependence of mobility upon molecular weight and chemical constitution in the case of organic anions. Direct determinations were being carried out in the early summer of 1914, and the experiments are now being completed. The values taken here must be substantially correct for the true ions, but, as we shall see in Section XI below, a still higher mobility must be ascribed to the ionic micelle. The concentrations of potassium or sodium ions thus deduced from the conductivity measurements are given in Tables VI and VII.

Table VI.—Concentration of Potassium Ions in Salts at 90°.

Weight normality.	Stearate, C_{18}.	Palmitate, C_{16}.	Myristate, C_{14}.	Laurate, C_{12}.	Caprate, C_{10}.	Caprylate, C_8.	Caproate, C_6.	Acetate, C_2.
0·2 N	0·072	0·080	0·094	0·103	0·135	0·135	0·140	0·145
0·5 N	0·205	0·202	0·243	0·262	0·278	0·298	0·310	0·324
0·75 N	0·305	0·345	0·366	0·384	0·399	0·389	0·426	0·454
1·0 N	0·408	0·446	0·489	0·515	0·521	0·527	0·523	0·582
1·5 N	—	—	—	0·696	—	0·728	—	0·800
2·0 N	—	—	—	0·885	—	0·898	—	1·01

Table VII.—Concentration of Sodium Ions in Salts at 90°.

Weight normality.	Stearate, C_{18}.	Palmitate, C_{16}.	Myristate, C_{14}.	Laurate, C_{12}.	Acetate, C_2.
0·2 N	0·053	0·079	0·085	0·099	0·140
0·5 N	0·166	0·195	0·216	0·239	0·303
0·75 N	0·272	0·286	0·324	0·350	0·409
1·0 N	0·386	0·369	0·405	0·455	0·511
1·5 N	0·533	0·553	0·543	0·615	0·664

By subtracting the values in Tables VI and VII from those in Tables IV and V we arrive at Tables VIII and IX, which give the concentrations of all the crystalloidal constituents other than potassium or sodium ions. The remainder of the soap must of course be colloid, and the values for this are given in Tables X and XI.

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* 'Trans. Chem. Soc.,' vol. 105, p. 435 (1914).

Table VIII.—Concentration of Crystalloidal Constituents other than K at 90°.

Weight normality.	Stearate, C_{18}.	Palmitate, C_{16}.	Myristate, C_{14}.	Laurate, C_{12}.	Caprate. C_{10}.	Caprylate, C_8.	Caproate, C_6.	Acetate, C_2.
0·2 N	0·14	0·17	0·18	0·21	0·20	0·22	0·21	0·24
0·5 N	0·15	0·19	0·23	0·28	0·36	0·43	0·43	0·63
0·75 N	0·08	0·11	0·19	0·24	0·47	0·58	0·67	
1·0 N	0·01	0·05	0·09	0·15	0·56	0·72	0·85	1·20
1·5 N	—	—	—	0·05				
2·0 N	—	—	—	0·11	—	0·74		

Table IX.—Concentration of Crystalloidal Constituents other than Na at 90°.

Weight normality.	Stearate, C_{18}.	Palmitate, C_{16}.	Myristate, C_{14}.	Laurate, C_{12}.	Acetate, C_2.
0·2 N	0·18	0·19	0·20	0·23	
0·5 N	0·20	0·22	0·28	0·34	0·63
0·75 N	0·18	0·21	0·26	0·31	
1·0 N	0·09	0·15	0·20	0·25	1·23
1·5 N	−0·20	−0·11	0·02	0·07	

Table X.—Concentration of Total Colloid in Potassium Salt Solution at 90°.

Weight normality.	Stearate, C_{18}.	Palmitate, C_{16}.	Myristate, C_{14}.	Laurate, C_{12}.	Caprate, C_{10}.	Caprylate, C_8.	Caproate, C_6.	Acetate, C_2.
0·2 N	0·06	0·03	0·02	−0·01	0·00	−0·02	−0·01	−0·04
0·5 N	0·35	0·31	0·27	+0·22	0·14	+0·07	+0·02	−0·13
0·75 N	0·69	0·64	0·56	0·51	0·28	0·17	0·08	
1·0 N	0·99	0·95	0·91	0·85	0·44	0·28	0·15	−0·20
1·5 N	—	—	—	1·55				
2·0 N	—	—	—	1·89	—	1·26		

Table XI.—Concentration of Total Colloid in Sodium Salt Solutions at 90°.

Weight normality.	Stearate, C_{18}.	Palmitate, C_{16}.	Myristate, C_{14}.	Laurate, C_{12}.	Acetate, C_2.
0·2 N	0·02	0·01	0·00	−0·03	
0·5 N	0·30	0·28	0·22	+0·16	−0·13
0·75 N	0·57	0·54	0·49	0·44	
1·0 N	0·91	0·85	0·80	0·75	−0·23
1·5 N	(1·70)	1·61	1·48	1·43	

The first point to notice is that every 1·0 N solution, from the caproate (C_6) upwards, contains colloid. In the case of the caproate only 15 per cent. of the soap is present in this form, while in the potassium stearate solution 99 per cent. is colloid. This is in accordance with the results of former work from this laboratory on the appearance, washing power, density, and conductivity of soap solutions. The great increase in amount of colloid takes place in passing from the caprate (C_{10}) to the laurate (C_{12}), when it about doubles.

Again, in every case the amount of colloid falls off steadily and very rapidly with decrease of concentration. It appears to become inappreciable as measured at N/5 laurate; but an error of 0·01° in the dew point is equal to 10 per cent. in the concentration in this dilute solution, and it is probable that a small amount of colloid is still present.

It is necessary to consider the validity of this comparison of osmotic with conductivity data. It is undoubtedly the case that the osmotic values are too high, presumably, as already mentioned, on account of hydration of the solute (see Section IV above). The ebullioscopic method shows this particularly, for Beckmann, by this method, obtained values corresponding to dissociations which, in the case of sodium acetate, actually increased from 78 per cent. in N/4 solution to 95 per cent. in 1·9 N solution. The apparent dissociations of potassium and sodium chlorides pass through minima of 76 and 84 per cent. at about N/10, rising to 89 per cent. for 2·5 N KCl, and to the impossible value of 106 per cent. for 2·1 N NaCl.

The dew-point method is more reliable than the ebullioscopic method, since the latter measures only a very rough dynamic thermal equilibrium instead of a true static one. But even so, the dissociation for sodium acetate deduced from the conductivity falls short of the osmotic activity by 20 to 23 per cent. Were this deviation entirely due to hydration, seven or eight molecules of water would have combined with the acetate and its ions, a not improbable result in the light of other evidence.

On the other hand, the results of conductivity measurements are definitely too low, on account of the retarding influences of viscosity on the mobility of ions.

VIII. *The Evidence for the Existence of the Ionic Micelle.*

For convenience we shall discuss one particular example first, taking for this purpose the 1·0 N potassium stearate solution measured in Table I above. This solution has at that temperature of 90° an equivalent conductivity of 113·4 reciprocal ohms,* that of 1·0 N potassium acetate being 176·9 at the same temperature. It is evident that in this concentration the stearate conducts about two-thirds as well as the acetate itself, and that it must be recognised as an excellent conductor. Further, the concentration of free hydroxyl ion is only 0·002 N, which is quite negligible for our present purpose.

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* 'Trans. Chem. Soc.,' vol. 105, p. 424 (1914).

Taking the conductivity of potassium stearate for complete dissociation as $188 + 90 = 278$ mhos, as in Table VIII above, the concentration of potassium ion is calculated as $113/278 \times 1{\cdot}00$ N $= 0{\cdot}41$ N.

Now in Tables I and V the experimental result is that the sum total of all crystalloidal substances present in 1·00 N solutions such as K Str., $K^{\cdot}$ and $Str.'$ is 0·42 normal. Of this, then, 0·41 has to be taken for the potassium ion $K^{\cdot}$, leaving only 0·01 normal to include everything else. Instead of a total of 0·01 normal, at least 0·42 would have been required for the stearate ion if present, and a further 0·58 for the normal un-ionised material. Thus practically all of the negative ion must be in a colloidal form, in addition to the whole of the un-ionised material as well.

Apart from 0·41 N potassium ion, the whole of the stearate, including whatever carries the equivalent of this large amount of electricity, must be colloid and not simple unpolymerised stearate of any sort.

This evidence for the existence of the ionic micelle is not affected by varying the assumption with regard to the mobility of the carriers of the negative electricity within admissible limits. Thus, if we take the mobility as zero, ascribing all the conductivity to the potassium ion, the concentration of the latter would have to be 0·60 N; but the osmotic pressure is that of 0·42 N total crystalloid as a maximum, and this enormous amount of positive electricity has to be counterbalanced by an equal number of negative charges. If the negative carriers were credited with the same mobility as the acetate ion, 116 mhos, the concentration of potassium ion works out at 0·37 N, leaving only 0·07 N crystalloid to include 0·37 N stearate ion if present, in addition to any unpolymerised neutral soap. In Section X it will be shown that it is necessary to ascribe to the ionic micelle a mobility twice as great as that of the true stearate ion and equal to that of the potassium ion itself.

IX. *An Explanation of the Ionic Micelle on Mechanical Grounds.*

What is essentially new in the conception of a mobile micelle is the mechanism by which the micelle is built up round an aggregate of simple stearate ions which still retain their original electrical charges.

In the study of such electrolytic colloids as the proteins, it has long been assumed that an ion could be colloidal or associated with colloidal matter, but that was chiefly because quite enormous values are taken for the molecular weights of proteins, and molecules of such bulk must be expected to behave like colloids. Only a relatively low conductivity has ever been ascribed to them.*

The conception of these highly mobile, heavily hydrated micelles was originated by one of us in a 'General Discussion on Colloids and Viscosity,' held by the Faraday Society in 1913.† It was put forward to remove one of the chief difficulties in interpreting the properties of acid and alkali albumens, since it reconciles their enormous viscosity with their quite good conductivity.

Stokes's law applied to a sphere of radius a moving through a liquid of viscosity η may be expressed as follows:

$$V = \frac{F}{6\pi\eta a}$$

where V is the velocity caused by the action of a force F. Perrin and others have shown that this law applies to colloidal particles. In conductivity experiments, the force F is due to the electric charge on the ion, which is 96,540 coulombs per gram ion.

If this charge could be varied without other alteration of the ion, the driving force, velocity, and mobility or conductivity would vary in direct proportion.

If, on the other hand, a number of ions, say a dozen, were to coalesce, the resulting particles would be driven by a force equal to 12F. The velocity would not be proportionally great, for the radius of the sphere would now be increased by $a \times \sqrt[3]{12} = 2{\cdot}3a$. The new velocity would therefore be

$$\frac{12}{2{\cdot}3b} = 5{\cdot}2V.$$

This five-fold increase in mobility of the aggregate as compared with the separated ions would in practice be counterbalanced by the effect of the greatly enhanced electrostatic potential of the aggregate in attracting water molecules and other material, so that such an aggregate would become a heavily hydrated micelle. This great hydration would usually more than offset the extra mobility expected, and the result would be a colloidal particle of somewhat less mobility than a rather slow true ion. The hydration accounts for the enormous mechanical viscosity observed in all the systems mentioned and also for its variation with the concentration of the constituents, etc. Such hydration has for other reasons been commonly deduced by workers in this field.

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* It is a well-known and striking fact that many mechanical suspensions as well as colloidal particles have an actual mobility in the electrical field comparable with that of an ion. This has not, however, been associated with high conductance, for it has been generally explained on the Helmholtz conception of the shearing of an electrical double layer, water upon water, not on the assumption of such high electrical charge as we are here forced to recognise. Thus high mobility has not meant high conductivity, although both must be attributed to an ionic micelle.

† 'Trans. Faraday Soc.,' vol. 9, p. 99 (1913); 'Kolloid-Zeitschr.,' vol. 13, p. 56 (1913).

X. *The Constitution of Dilute Solutions of Soap.*

On account of the limitations of this method, N/5 soap solutions were the most dilute investigated. The result of measurements with 0·20 N potassium palmitate solution at 90° was as follows:—

Lowering of dew-point = rise of boiling-point at 90° = 0·12°.
Hence total concentrations of all ions and molecules present = 0·25 N.

Now the molar conductivity of N/5 potassium palmitate at 90° is 111·0 reciprocal ohms. If the conductivity at infinite dilution is 304, the concentration of potassium ions is 0·072 normal; if it be 278, the concentration is 0·080 normal K′.

Hydrolysis does not affect this result by more than about 2 per cent., which may be neglected for our present purpose.

Taking the second result, K = 0·080 N, total crystalloids present being 0·25 N, this leaves a concentration of 0·25 − 0·08 = 0·17 N crystalloids other than potassium ion. The total undissociated soap is 0·200 − 0·080 = 0·120 N. Thus, even if all the undissociated soap here is in simple crystalloidal form, there is still 0·17 − 0·12 = 0·05 normal crystalloid to account for, and this must be simple palmitate ions, since the hydroxyl ions have been shown to be only about 0·01 normal. The small balance of 0·03 is all that can be colloid.

Whether this relatively small amount of colloid is due to remaining micelle or to neutral colloid will be discussed below. The point to notice is that not more than a quarter of the undissociated palmitate, nor more than three-eighths of the palmitate ion may be in colloidal form. If there be some of each in colloidal form, this amount has to be divided up between them, so as not to exceed a total of 0·03 normal.

It is quite clear that in N/5 palmitate solution the breakdown of the colloid has gone moderately far, and that further dilution would rapidly complete it. In other words, we have a clear case of transition from colloid to crystalloid in the same solution, depending only on the concentration, and forming a true, stable, reversible equilibrium in each concentration. That a colloid can thus enter into true equilibria would appear to be of great importance for the theory of colloids.

XI. *The Mobility and Hydration of the Ionic Micelle.*

The results deduced in Tables V—XII are based upon a provisional assumption that the conductivity of the ionic micelle is equal to that of the fatty ions it has replaced.

However, the data in Tables IX—XII for 1·5 N solutions of potassium laurate, sodium stearate, and sodium palmitate show that the osmotic effect is less than that required upon this basis for the potassium or sodium ion alone. This cannot be due to the fact that uncorrected osmotic data always appear too high and conductivity data too low, as was pointed out in Section VII above, for this circumstance operates in the reverse direction from that required to explain the present data for these three solutions.

To reconcile the osmotic effect with the observed conductivity, it is therefore necessary to ascribe to the ionic micelle in these 1·5 N solutions a mobility at least twice as great as that of the true ion it has replaced. Thus, instead of a mobility of 90 mhos, the value in these concentrations must be about equal to that of the potassium ion, which is 188 mhos.

An alternative which we reject is the assumption of a positive as well as a negative micelle to replace some of the potassium ion. It is not in accordance with what we know of the behaviour of colloids that two oppositely charged colloids should be simultaneously present in the free condition. Experiments which were in progress in 1914, and are now being completed, afford direct measurements of the concentration of potassium and sodium ions present, and therefore remove any uncertainty upon this point.

Our conception is that the mobility of the ionic micelle increases with concentration. Important confirmation is given, for example, by the conductivity. It is definitely a fact that the higher soap solutions, quite apart from the small amount of free alkali present, exhibit minimum conductivity in tenth or fifth normal solutions. (Previous papers from this Laboratory, also confirmed by the experiments of F. Goldschmidt and co-workers.)* In higher concentrations the conductivity rises appreciably up to half normal or normal solutions, where a maximum is observed. This is direct evidence that the ionic micelle which is replacing the fatty acid ion is a better conductor than that ion. The ultimate falling off in very concentrated solutions is the effect of the diminishing dissociation of the electrolytic colloid.

The higher soaps are the most colloidal, and the potassium soaps contain more colloid than the sodium salts. It is just these cases that exhibit the minimum in decinormal solution. The better conducting and less colloidal potassium laurate (C_{12}), and the sodium soaps, do not show a minimum until fifth normal solution is attained.

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* Ubbelohde and Goldschmidt, 'Handbuch der Oele und Fette,' vol. 3, Leipzig (1910–11); 'Zeitschr. Electrochem.,' vol. 18, p. 380 (1912); 'Kolloid-Zeitschr.,' vol. 12, p. 18 (1913); 'Kolloid-Chem. Beihefte,' vol. 5, p. 427 (1914).

Again, the lowering of vapour pressure passes through a maximum in normal solution, where the total concentration of crystalloid is at a maximum. Diminishing hydration and diminishing dissociation of the colloidal electrolyte combine to reduce the lowering of vapour pressure, and it therefore falls to the minimum observed in one and a half normal solution. There must be a limit to this action, as the proportion of total water present gets less, hence the minimum at 1·5 normal.

Diminishing hydration with increasing concentration of the micelle, or some other alteration in the formula of the micelle, follows again from the principle of mass action, for otherwise within a very narrow range of concentration the colloidal electrolyte would pass completely into an undissociated form and no longer conduct.

The diminishing hydration is not due to water becoming scarce, for the fact that the vapour pressure of 1·5 N solution is greater than 1·0 N solution means that water is more available in the former than in the latter. The hydration being less in 1·5 N, where the water is most active and available, can only be explained by some such alteration in the formula or structure of the micelle as the increasing proportion of undissociated soap in it.

Other evidence in support of this assumption will be discussed below in Sections XII and XIV. Decrease of hydration with rise of temperature explains other conductivity data of the previous papers; this will be discussed in a separate communication.

Reverting to the consideration of Tables VIII–XI, these appear then to be substantially correct for all dilute solutions. For most solutions, they probably indicate minimum values for the amounts of colloid present. For the most concentrated solution of the higher soaps, the formation of colloid is necessarily less than that given in the Tables, but these solutions appear to contain little else than colloid, together with potassium or sodium ion.

XII. *The Formula of the Ionic Micelle.*

Various views may well be taken with regard to the formation of the ionic micelle. The simplest is to consider it as an agglomeration of palmitate ions, heavily weighted by water, a complex solvate :—

$$(P')_n \,.\, (H_2O)_m. \qquad (1)$$

The second and chief of the possible alternative formulæ, and that which appears to us most plausible, is that all or nearly all the colloid collects in the ionic micelle :—

$$(NaP)_x \,.\, (P')_n \,.\, (H_2O)_m. \qquad (2)$$

Other hypotheses, based upon assumption of extensive hydrolysis, compensated by nearly quantitative sorption of the hydroxyl ion, give identical composition, with a different structure. Such formulæ, however, have been excluded through direct measurements of the sorption of sodium hydroxide, which is found to be only very small; some of the data for this have already been published. Similarly, the existence of such a hydrogen soap as Reychler's cetyl sulphonic acid, in which hydrolysis is out of the question, renders such strained conceptions valueless.

That a water sphere should collect around these enormous electrical charges is as inevitable as the collection of a droplet of water round an electron in saturated water vapour; but, if the undissociated colloid also joins in, it leads to formula (2).

In formula (1) above, driving back the dissociation does not so much alter the composition of the ionic micelle, but, instead, replaces it by the neutral colloid produced. This hypothesis, that the micelle contains but little of the undissociated soap, which exists independently as a neutral colloid, can be made to account for the chief facts relating to soap solutions, although not so readily as formula (2). In dilute solutions, as was shown in previous sections, neutral undissociated soap does exist independently, but in simple crystalloidal form.

Formula (2) presents a general scheme for the composition of the micelle, which would alter continuously with concentration, or upon the addition of salts. Thus, in very concentrated solution, or in the presence of large amounts of another electrolyte, such as sodium hydroxide (see below), the soap must be nearly all colloid, of approximately the composition

$$x\mathrm{NaP}\,.\,m\mathrm{H_2O}. \qquad (3)$$

This change of composition upon increasing the concentration would, as suggested in Section XI, serve to explain the surprisingly great mobility and diminished hydration of the micelle in concentrated solution, where the mobility is more than double that which would have been predicted from the properties of complex ions hitherto studied.

A further argument for the conception embodied in formula (2) is the divergence in behaviour between the potassium and sodium soaps. This cannot be so readily explained if the micelle in both is identical, as is required for formula (1). But, according to formula (2), it becomes quite possible that the sodium and potassium soap micelles should differ distinctly, as they do.

XIII. *Possible Limits of Concentration of Ionic Micelle Present.*

We have shown how the approximate values of the concentrations of the total crystalloid and total colloid can be arrived at. We have now to attempt to allocate the total colloid between neutral colloid and micelle and the total crystalloid between undissociated soap, sodium or potassium ion, and simple fatty ion. This is at present possible only within the definite limits set out in the Tables below.

For the purpose of the present section, the distinction will be drawn as between the agglomerated palmitate ions in the ionic micelle and the remainder of the colloid, termed neutral colloid. It is clear that the numbers retain their full significance, whether formula (1) above, or the more probable formula (2), is accepted, where part or most of the neutral colloid is taken up by the ionic micelle

$$(P')_n \, . \, (H_2O)_m \, . \, (NaP)_x. \qquad (2)$$

The data given represent in both cases the amount of soap present as $(P')_n$ in the ionic micelles. The concentrations of "neutral colloid" set out in the Tables include the soap present as $(NaP)_x$ in the ionic micelles.

The results, which are recorded in Tables XIII–XVI, are based upon the two extreme possibilities. The first figure of each pair allocates the total colloid as far as possible to ionic micelle; this cannot, of course, exceed the concentration of potassium or sodium ions, and any excess above this must necessarily be ascribed to neutral colloid. This procedure fixed the minimum possible values for simple fatty acid ion P′, and also the maximum possible amount of simple undissociated soap, NaP.

The second figure in each case gives the opposite extreme consistent with our measurements, allotting the total colloid to neutral colloid as far as possible; the maximum limit to the neutral colloid here is the total amount of undissociated soap obtained by subtracting the concentration of potassium or sodium ions from the total concentration of the solution; any excess of colloid must be recognised as ionic micelle.

Table XII.—Limits of Concentration of Colloidal Constituents of K Salts.

Weight normality.	Stearate, C_{18}.	Palmitate, C_{16}.	Myristate, C_{14}.	Laurate, C_{12}.	Caprate, C_{10}.	Caprylate, C_8.	Caproate, C_6.
Agglomerated Ions in the Ionic Micelle.							
0·2 N	0·06–0·00	0·03–0·00	0·02–0·00	0	0	0	0
0·5 N	0·21–0·06	0·20–0·01	0·24–0·01	0·22–0·00	0·14–0·00	0·06–0·00	0·02–0·00
0·75 N	0·31–0·23	0·35–0·24	0·37–0·18	0·38–0·14	0·28–0·00	0·17–0·00	0·08–0·00
1·0 N	0·41–0·40	0·45–0·40	0·49–0·40	0·52–0·37	0·44–0·00	0·28–0·00	0·15–0·00
1·5 N	—	—	—	0·70–0·75			
2·0 N	—	—	—	0·89–0·78	—	0·90–0·16	
“Neutral Colloid.”							
0·2 N	0·00–0·06	0·00–0·03	0·00–0·02	0·00	0·00	0·00	0·00
0·5 N	0·14–0·29	0·11–0·30	0·03–0·26	0·00–0·22	0·00–0·14	0·00–0·07	0·00–0·02
0·75 N	0·38–0·46	0·29–0·40	0·19–0·38	0·13–0·37	0·00–0·28	0 00–0·17	0·00–0·08
1·0 N	0·58–0·59	0·50–0·55	0·42–0·51	0·33–0·48	0·00–0·44	0·00–0·28	0·00–0·15
1·5 N	—	—	—	0·85–0·80			
2·0 N	—	—	—	1·00–1·11	—	0·36–1·10	

Table XIII.—Limits of Concentration of Crystalloidal Constituents of K Salts at 90°.

Weight normality.	Stearate, C_{18}.	Palmitate, C_{16}.	Myristate, C_{14}.	Laurate, C_{12}.	Caprate, C_{10}.	Caprylate, C_8.	Caproate, C_6.	Acetate, C_2.
Simple Fatty Acid Ion.								
0·2 N	0·01–0·07	0·05–0·08	0·07–0·09	0·11–0·10	0·14–0·14	0·15–0·14	0·15–0·14	0·19–0·15
0·5 N	0·00–0·15	0·00–0·19	0·00–0·23	0·04–0·26	0·14–0·28	0·23–0·30	0·29–0·31	0·45–0·32
0·75 N	0·00–0·08	0·00–0·11	0·00–0·19	0·00–0·24	0·12–0·40	0·22–0·39	0·35–0·43	0 –0·45
1·0 N	0·00–0·01	0·00–0·05	0·00–0·09	0·00–0·15	0·08–0·52	0·25–0·53	0·37–0·52	0·78–0·58
1·5 N	—	—	—	0·00–0·05	—	—	—	0 –0·80
2·0 N	—	—	—	0·00–0·11	—	0·00–0·74	—	0 –1·01
Simple Neutral Undissociated Salt.								
0·2 N	0·13–0·07	0·12–0·09	0·11–0·09	0·10–0·11	0·06–0·06	0·07–0·08	0·06–0·07	0·01–0·05
0·5 N	0·15–0·00	0·19–0·00	0·23–0·00	0·24–0·02	0·22–0·08	0·20–0·13	0·19–0·17	0·05–0·18
0·75 N	0·08–0·00	0·11–0·00	0·19–0·00	0·24–0·00	0·38–0·07	0·36–0·19	0·32–0·24	0 –0·30
1·0 N	0·01–0·00	0·05–0·00	0·09–0·00	0·15–0·00	0·48–0·04	0·47–0·19	0·48–0·33	0·22–0·42
1·5 N	—	—	—	−0·05–0·00	—	—	—	0 –0·75
2·0 N	—	—	—	0·11–0·00	—	0·74–0·00	--	0 –0·99

Table XIV.—Limits of Concentration of Colloidal Constituents of Na Salts at 90°.

Weight normality.	Stearate, C_{18}.	Palmitate, C_{16}.	Myristate, C_{14}.	Laurate, C_{12}.	Acetate, C_2.
			Agglomerated Ions in the Ionic Micelle.		
0·2 N	0·02–0·00	0·01–0·00	0·00–0·00	−0·03–0·00	0·00–0·00
0·5 N	0·17–0·00	0·20–0·00	0·22–0·00	0·16–0·00	−0·03–0·00
0·75 N	0·27–0·09	0·29–0·08	0·32–0·06	0·35–0·04	0·00–0·00
1·0 N	0·39–0·30	0·37–0·22	0·41–0·21	0·46–0·21	−0·23–0·00
1·5 N	0·53–0·73	0·55–0·66	0·54–0·52	0·62–0·55	0·00–0·00
			"Neutral Colloid."		
0·2 N	0·00–0·02	0·00–0·01	0·00–0·00	0·00–0·00	0·00–0·00
0·5 N	0·13–0·30	0·08–0·28	0·00–0·22	0·00–0·16	0·00–0·13
0·75 N	0·30–0·48	0·25–0·46	0·17–0·43	0·09–0·40	0·00–0·00
1·0 N	0·52–0·61	0·48–0·63	0·39–0·59	0·29–0·54	0·00–0·23
1·5 N	0·17–0·97	1·06–0·95	0·94–0·96	0·81–0·88	0·00–0·00

Table XV.—Limits of Concentration of Crystalloidal Constituents of Na Salts at 90°.

Weight normality.	Stearate, C_{18}.	Palmitate, C_{16}.	Myristate, C_{14}.	Laurate, C_{12}.	Acetate, C_2.
			Simple Fatty Acid Ion.		
0·2 N	0·03– 0·05	0·07– 0·08	0·09–0·09	0·13–0·10	0·00–0·00
0·5 N	0·00– 0·17	0·00– 0·20	0·00–0·22	0·08–0·24	0·43–0·30
0·75 N	0·00– 0·18	0·00– 0·21	0·00–0·26	0·00–0·31	0·00–0·00
1·0 N	0·00– 0·09	0·00– 0·15	0·00–0·20	0·00–0·25	0·74–0·51
1·5 N	0·00– −0·20	0·00– −0·11	0·00–0·02	0·00–0·07	0·00–0·00
			Simple Neutral Undissociated Salt.		
0·2 N	0·15– 0·13	0·12– 0·11	0·11–0·11	0·10–0·13	0·06–0·06
0·5 N	0·20– 0·03	0·22– 0·02	0·28–0·06	0·26–0·10	0·20–0·33
0·75 N	0·18– 0·00	0·21– 0·00	0·26–0·00	0·31–0·00	0·34–0·34
1·0 N	0·09– 0·00	0·15– 0·00	0·20–0·00	0·25–0·00	0·49–0·72
1·5 N	−0·20– 0·00	−0·11– 0·00	0·02–0·00	0·17–0·10	0·84–0·84

Discussion on the Theory of Relativity.

(February 5, 1920.)

Mr. J. H. Jeans: During the last century, two great dominating principles of physics emerged—the Conservation of Energy and the Second Law of Thermodynamics. The present century has already added a third member to this list, the principle of Relativity, which we are to discuss to-day. The three principles have in common that they do not explain how or why events happen; they merely limit the types of events which can happen. Thus the principle of Conservation of Energy shows that water cannot flow uphill; the Second Law of Thermodynamics shows that heat cannot flow from a cold body to a hot; the principle of Relativity shows that a planet cannot describe a perfect ellipse about the sun as focus. But it would be as unreasonable to expect the principle of Relativity to explain why a planet describes an orbit or how a ray of light is propagated as it would to propound the same questions to the principle of Conservation of Energy or the Second Law of Thermodynamics. All three principles deal with events, and not with the mechanism of events.

The main interest of the new theory, however, is not merely that it discloses a new universal principle; it is rather that it discloses a new universe. Our former belief that the foundations of science had been laid for all time has been shattered; we now find that the land on which we had built was largely a mirage. New and mysterious continents appear for science to explore, but it is not for the theory of Relativity to explore them. The methods of that theory are destructive rather than constructive, and, when the theory predicts a positive result, it is invariably for the same reason, namely, that a process of exhaustion shows that any other result would be impossible.

Historically, the theory had its origin in the famous experiment of Michelson and Morley. Light sent from a source O to a mirror P was reflected back to O, and it was found that the average to-and-fro velocity was the same for all directions of OP in space. To those who believed in a fixed ether through which light propagation took place, the result was surprising, for, on the ether-hypothesis, the average to-and-fro velocity would depend on the orientation of OP relative to the earth's motion through the ether.

As Ritz and others have pointed out, the result is intelligible enough if we adopt an emissive or corpuscular theory of light, but such a theory is difficult to reconcile with the majority of electromagnetic phenomena, and seems to be definitely negatived by recent experiments of Majorana. Majorana finds that the velocity of light is not altered when it is reflected by a moving mirror, and neither is it altered when emitted by a moving source.

Thus we have almost conclusive proof of the truth of a hypothesis, first put forward by Einstein in 1905, which has formed the foundation of the whole theory of relativity. The hypothesis is that light from any source appears to any observer to travel always with the same velocity C, or, more concisely, the wave-surface is a sphere surrounding the observer. There is a much better justification for this hypothesis than is to be found in the experiments of Michelson-Morley and Majorana; it is that the hypothesis explains a vast number of physical phenomena, and has, so far, not been found inconsistent with a single one.

Suppose that two observers, S, S′, move with different velocities, but happen to coincide at the origin at an instant $t = 0$, at which a light signal is sent out from the origin. A wave-surface will be formed, and each observer will assert that it is spherical, and that he is at its centre. Since a sphere cannot have two different centres at once, we can only conclude that the two observers mean different things by their statements, or, in other words, they are using different co-ordinates. The Fitzgerald-Lorentz contraction hypothesis had prepared the ground for this conception. If light appears both to S and S′ to travel in straight lines with uniform velocity, then the co-ordinates x, y, z, t used by S and x', y', z', t' used by S′ must be connected by a linear transformation, and $x^2+y^2+z^2-C^2t^2$ must transform into $x'^2+y'^2+z'^2-C^2t'^2$. It follows that, in a four-dimensional continuum having x, y, z and $\tau\,(=iCt)$ as rectangular co-ordinates, the axes of x', y', z', τ' must be derived from those of x, y, z, τ by a pure rigid-body rotation.

Corresponding to a rotation θ in the x, τ plane, the equations of transformation are readily seen to be

$$x' = \beta(x-ut), \quad y' = y, \quad z' = z, \quad t' = \beta(t-ux/C^2),$$

where $\beta = \cos\theta = (1-u^2/C^2)^{-\frac{1}{2}}$ and u is the relative velocity of the two observers. These are precisely the equations of the famous Lorentz-transformation. Before the appearance of Einstein's theory, Lorentz had already discovered these equations as the condition that all optical and electromagnetic phenomena should be the same for all observers, regardless of their relative velocities. These equations explain and predict a great number of physical phenomena,—*e.g.*, the variation of mass with velocity, electromagnetic forces in ponderable media, Fizeau's water-tube experiment. Nothing in physics has yet been found to be inconsistent with them. The theory of Relativity insists upon the truth of the equations, at any rate in the absence of a gravitational field, but it tells us nothing as to their physical interpretation. The earliest attempt at an explanation was the Lorentz-Fitzgerald contraction hypothesis, but its inadequacy is easily discovered. Following Ehrenfest, let us imagine a cart wheel revolving about an axle at rest in the ether which is postulated by the contraction theory. Each element of the rim moves with the same velocity u, and so is contracted in a uniform ratio $1/\beta$, but the spokes, moving only at right angles to their length, undergo no contraction at all. If the contraction-theory were true, a rotating wheel of radius a would have a rim of length $2\pi a/\beta$.

The apparent paradox is resolved when we think in terms of the four-dimensional continuum, and only then. A point in the continuum is an "event." To each observer separately an "event" is a point (x, y, z) at an instant (t), but we must remember that different observers divide the continuum into space and time in different ways. To one observer, the interval between two events is so much time and so much space, but another observer estimates both the time and space differently. The interval between a man's birth and death may be estimated by S as 1000 miles and 75 years, but S′ may call it millions of miles and 76 years. The only final objective measurement is that of a single range in the continuum; its square is one million square miles minus the square of 75 light-years.

The contraction hypothesis expressed in terms of the continuum immediately becomes consistent and complete. What S calls a length l, is resolved by S′ into $l \sec\theta$ or l/β along S′'s axis of length, and $l \tan\theta$ along S's axis of τ, representing a time interval lu/C^2. The Fitzgerald contraction in length is compensated by an expansion in time.

The successive positions of a particle or a ray of light will be represented by a continuous series of points in the four-dimensional continuum, forming what Minkowski calls the "world-line" of the particle or ray. The analytical equation of this "world-line" is an integral of the equations of motion of the particle or light-ray. The Newtonian law of motion is that the world-line of a particle acted on by no forces is a straight line. The equation of this straight line may be put in the invariant form $\delta\int ds = 0$, this being of course invariant as regards all rotations of the axes and so being the same for all observers.

The general relativity-condition is that *all* the laws of nature shall be invariant as regards different sets of orthogonal axes in the continuum. If any single law of nature shows a special connection with any special set of axes, we shall have an objective means of identifying one special set of axes, and this leads at once to a possibility of determining absolute velocity in space. As a matter of experiment, the laws of light and electromagnetism are found to conform to the relativity-condition, with the consequence that no absolute velocity can be revealed by optical or electromagnetic means. But it is easily seen that the Newtonian law of gravitation mm'/r^2 does not conform to this condition, so that if the Newtonian law were true, it would be possible to determine absolute motion in space. Sir O. Lodge, assuming the Newtonian Law to be true, determined what velocity of the Sun in space would be required to account for the observed motion of the planet Mercury, but Prof. Eddington showed that quite different velocities would be determined from the motions of the other planets. Einstein's first theory of gravitation proceeded by simply modifying the Newtonian law so that it conformed to the condition of invariance, but this modified law predicted a motion of the perihelion of Mercury equal to only one-sixth of the amount observed, and a gravitational deflection of light equal only to about half of that discovered at the recent eclipse.

Einstein's second theory is of a much more radical nature. He does not merely modify the expression of the laws of nature in the four-dimensional continuum; he modifies the continuum itself. The continuum is supposed to be affected with twists and kinks centering round those values of x, y, z, and t which represent positions of matter at different instants. Gravitation is no longer a physical force; it is merely our interpretation of the fact that the continuum is not Euclidean; parallel lines meet or diverge, so that particles projected along parallel lines may in time collide with one another. Their collision is a consequence of the special metrical properties of the space, but we have up to now ascribed it to a supposed attractive force which we have called gravitation. According to Einstein's theory it is no more accurate to say that the earth attracts a falling body than to say that the pockets of an uneven billiard table repel the balls.

A somewhat imperfect analogy will perhaps explain the fundamental conceptions of Einstein's theory. Let us imagine a race of cave-dwellers shut away for ever from the earth's surface, and therefore having no reason to suspect either the roundness or rotation of the earth. To them, gravitation would appear a simple matter; they would notice that bodies fell to the floor of their cave with a constant uniform acceleration, and they might ascribe this to a "force" of gravity, acting always in one direction, which they would call the vertical. To the cave-dwellers a system of mechanical laws identical with our Newtonian laws would seem quite consistent and plausible. The expression "at rest" would of course mean "keeping the same distance from the walls of the cave," and it would probably never occur to them that any more precise analysis or definition was needed.

Some day a cave-dwelling Foucault might try the experiment of suspending a weight from the roof of the cave and examining what orbit it would describe, when projected in any way. He would expect it to be an ellipse indefinitely repeated, but would find that it was an ellipse which rotated slowly in its own plane. The cave-dwellers might further mark out straight lines which satisfied all geometrical tests perfectly, but (as a consequence of the earth's rotation), refined experiments would show that light did not follow these straight lines.

The cave-dwellers would now have two reasons for doubting their simple laws. Light would appear to be deflected from straight lines, and orbits which ought to be recurrent ellipses would be found to be revolving ellipses. In the results of the recent Eclipse expedition and in the observed motion of Mercury, we have precisely similar reasons for doubting our simple laws, and the explanation of their failure which is suggested to us by Einstein is precisely of the same nature as that which might be suggested to the cave-dwellers by a troglodyte scientist. We have tacitly assumed fixed axes where nothing is fixed: we have formed wrong ideas of the nature of gravitation: and our definition of a straight line is interwoven with the ideas of an untrue system of geometry.

We are familiar with the conception of the gravity-acceleration on the earth's surface as being due partly to centrifugal force and partly to the earth's attraction. Our level surfaces are equipotentials under a potential

$$\frac{M}{r}+\tfrac{1}{2}\omega^2(x^2+y^2)$$

and we were taught in our youth that the first term represents real forces and the second term only fictitious forces. The recognition by the cave-dwellers that the second term represented only fictitious forces would remove their troubles with the Foucault experiment. The suggestion of generalised relativity is that the further recognition by us that both terms represent fictitious forces will remove the troubles which have so far centred round our Newtonian law of gravitation.

In the four-dimensional continuum already considered, the interval between two adjacent events is

$$(ds)^2=(dx)^2+(dy)^2+(dz)^2-C^2(dt)^2, \tag{A}$$

this being of course invariant for all observers. According to Einstein's generalised theory this expression is only true at an infinite distance from all gravitating matter. In the neighbourhood of matter it must be replaced by

$$(ds)^2=g_{11}(dx)^2+g_{22}(dy)^2+2g_{12}\,dx\,dy\ldots-g_{44}C^2(dt)^2, \tag{B}$$

in which the coefficients $g_{11}-1$, g_{12}, ... specify the gravitational field.

To see the meaning of this, imagine that our cave-dwellers had suspected their cave to be in rotation and so had transformed expression (A) to rotating axes. It would have to be replaced by

$$(ds)^2 = (dx)^2 + (dy)^2 + (dz)^2 + 2\omega y\, dx\, dt - 2\,\omega x\, dy\, dt - [C^2 - \omega^2 (x^2 + y^2)]\, dt^2, \quad \text{(C)}$$

Their old laws of motion, according to which particles and light rays described straight lines with uniform velocity, could be put in the form $\delta\int ds = 0$ with ds given by (A). They would find that the same equation with ds given by (C) would predict exactly the observed deflection of their light rays and would enable them to deduce the orbit of their Foucault experiment. With other values for g_{11}, etc., in (B) Einstein shows that the same law of motion $\delta\int ds = 0$ will remove our difficulties about the perihelion of Mercury and the deflection of light.

At first sight it might be thought that with so many adjustable constants, g_{11}, etc., this would be a foregone conclusion. But the values of g_{11}, etc., which conform to the relativity condition are practically limited to a single set, in which ds is given by

$$(ds)^2 = \gamma^{-1} (dr)^2 + r^2\, d\theta^2 + r^2 \sin^2\theta\, d\phi^2 - C^2 \gamma\, dt^2, \quad \text{(D)}$$

where γ stands for $1 - 2M/rC^2$. There are in reality no adjustable constants, and it was this circumstance which enabled Einstein to predict without any uncertainty the deflection of light to be expected. We notice that in both (C) and (D) the coefficient of dt^2 is

$$C^2 - 2 \times (\text{potential of apparent field of force}),$$

and when the coefficient of dt^2 is fixed, the others follow almost uniquely from the conditions of invariance.

A particle which is not acted upon by electromagnetic forces of any kind will have a world-line which is a geodesic (defined by $\delta\int ds = 0$) in the twisted space defined by (D). This world-line is the straightest line (if I may be permitted this use of words) which can be drawn in the space in question, but it will not be straight in the Euclidean sense. An observer who has been taught to think in terms of the conceptions of Euclid and Newton will expect the world-line to be a Euclidean straight line, and will ascribe its deviations from his ideas of straightness to the action of gravitational force.

Mathematicians are accustomed to be asked why they cannot express the new law of gravitational force in simple form. The answer is easy: there is no force, and therefore no law of force to be expressed. The laws of *motion* can be expressed in the simplest conceivable form, namely $\delta\int ds = 0$.

What, however, is meant by ds? The simplest interpretation is to regard it merely as a conventional algebraic symbol defined by (D). Then the law of motion predicts Mercury's orbit and light-deflection, but does not, I think, make any prediction about shift in the Fraunhofer lines. Einstein gives to ds a special interpretation in terms of time and space; for him ds is a line-element in a distorted space-time continuum. The hypothesis from which this special interpretation is derived requires inevitably, Einstein considers, a shift of the Fraunhofer lines towards the red, and I do not think we can dispute that he is right. It also requires us to believe in an objective curved four-dimensional space, and grave difficulties are disclosed by a consideration of the limits of this space. Indeed, the difficulties are so grave that, as Prof. Eddington has pointed out, Einstein is prepared to abandon the whole central principle of relativity in an attempt to remove them.

For myself, I have never felt convinced that any sufficient reason compels us to adopt Einstein's interpretation of ds. Fermat's law giving the path of a ray of light in an anisotropic refracting medium can be put in the form $\delta\int ds = 0$, where

$$(ds)^2 = k_{11}(dx)^2 + k_{22}(dy)^2 + 2k_{12}\,dx\,dy + \ldots,$$

but we should be led into terrible difficulties if we tried to interpret ds as a line element in a twisted three-dimensional space. I will hasten to add that I am aware that the cases are not parallel; the most I suggest is that the analogy of Fermat's law may justify us in hesitating before accepting Einstein's physical interpretation of ds. If we do not insist on Einstein's interpretation of ds, the theory becomes less rich and less inclusive, but at the same time less beset by difficulties. The reality of the four-dimensional continuum is, I think, beyond dispute, but the reality of the twists and kinks in it do not appear to be. Decisive knowledge as to the shift of the Fraunhofer lines would go far towards settling this question.

Prof. A. S. EDDINGTON: The sun's gravitational field has been summed up in the rather mysterious expression

$$ds^2 = -(1-2m/r)^{-1}dr^2 - r^2d\theta^2 - r^2\sin^2\theta d\phi^2 + (1-2m/r)\,dt^2.$$

I would like first to explain in a general way how the ordinary Newtonian attraction of the sun is here represented.

r is the distance from the sun and t the time (both being reckoned rather conventionally, so far as exact definition is concerned). If we want to make a graph of the motion of a particle, we take r and t as horizontal and vertical co-ordinates. I call such a representation a picture. I want to distinguish between a *picture* and a *map*. If we are given the latitudes and longitudes of places on the earth, we can make a picture by taking latitude and longitude as vertical and horizontal co-ordinates; but that does not give us a map. In any ordinary map of Europe the lines of longitude run obliquely, and the lines of latitude are curved. Why is this? Because the map aims at representing all the distances of places in their proper proportions. Distance is the important thing, which we want to represent correctly. Now, in the space-time round the sun, the interval ds is the important thing—the thing with an absolute significance in nature. We want to make a map, so that all the intervals are represented in their proper proportions; and the above formula gives us the rules for drawing the map. If I had time, I could show you in detail how to derive the shape of the r-lines and t-lines on the map, which may be compared with the longitude and latitude lines on a terrestrial map.

Now, the law of motion, whether gravitation is acting or not, is extremely simple—every particle describes a straight line on the *map*. Let us draw such a straight line. Now go back to the *picture*; we distort the whole figure till the r-lines and t-lines become vertical and horizontal, and the graph of the particle's track is then distorted into a curve—concave to the sun. We say the particle is attracted. This curving comes from the difference of the map and the picture, and it is the same phenomenon that is usually described as the force of the sun's gravitation.

There are two methods of exploring space and time. One is with a scale and clock; the other with moving particles and light-pulses. In each way we can find out the geometry of space-time. It is conceivable that the two methods might give different geometries, each true in its own sphere. If we had to make a choice, I think we should prefer the geometry of moving particles and light-pulses, because these are very simple things, whereas scales and clocks even of the simplest form have elaborate structure; another reason is that, in practice, moving particles and light-pulses give a very much more sensitive method. The astronomer uses this method; by his moving particles, the planets, and especially the planet Mercury, and by the light-pulses from stars during the solar eclipse, he has established that the geometry is summed up in the expression for ds^2 which I have already written. If you like to reject Einstein's theory altogether, and disagree with every idea in Mr. Jeans' exposition, that will not alter the fact that the formula is true experimentally to a certain high degree of approximation for the geometry of moving particles and light-pulses.

Is the geometry of scales and clocks the same? There are certain theoretical reasons for thinking it is—at least, to a degree of approximation sufficient for our purposes. But scales and clocks are so insensitive that only one rather crude test seems to be possible. That is to have a clock on the sun and a similar clock on the earth, and to compare them.

If the clocks are similar, they will each beat out similar values of the absolute thing, the interval; what they beat in time depends on how you measure time, because time is not absolute. If we measure time in the usual way for the solar system by t, and if our clocks are at rest so that r, θ, ϕ do not change during the vibration (dr, $d\theta$, $d\phi = 0$), then by the formula

$$ds^2 = \left(1 - \frac{2m}{r}\right) dt^2$$

so that

$$dt = ds/\sqrt{(1 - 2m/r)}.$$

Thus, if the two clocks measure equal values of ds, they will not measure equal values of dt. The solar clock, for which r is small, will have the longer period, dt.

In the actual experiment, two atoms are used for the clocks. We cannot, of course, determine the period of the solar atom directly; we have to measure the period of the waves emitted by it when they reach the earth. It turns out, however, that the period is carried to us unaltered—a result due to our judicious choice of the co-ordinate which we consider to be the time. I expect later speakers will deal with the results of this test.

Sir F. W. DYSON: Leverrier found that the perihelion of Mercury advances 43″ a century in excess of the amount produced by the action of the planets.

The following hypotheses have been advanced in explanation :—

(1) Oblateness of the sun.
(2) An intra-Mercurial planet.
(3) A ring of planets between Venus and Mercury, or between Mercury and the sun.
(4) Extended matter whose presence is indicated by the Zodiacal light.
(5) Alteration of the law of attraction from r^{-2} to $r^{(-2+\delta)}$ where $\delta = 0{\cdot}000{,}00016$.

Taking these in order, (1) would require the sun's equatorial diameter to be 0″·5 greater than its Polar diameter. Comparison with Jupiter, which rotates in 10 hours, while the sun rotates in 25 days, indicates an oblateness of less than one-tenth of this amount. Further, measures of the sun's diameter entirely negative this supposition.

(2) An intra-Mercurial planet has been carefully looked for in Eclipse Expeditions. Although stars down to the 9th magnitude have been photographed, no unknown body has been found.

(3) Such a ring would need to lie nearly in the plane of Mercury, or it

would affect the movement of the node as well as the apse. Mercury is highly inclined to the invariable plane of the planetary system. It is very unlikely that a ring of small bodies would be in the plane of Mercury, and it is not certain that a ring would be stable.

(4) The Zodiacal light extends to at least 90° from the sun. It is attributed to the reflection of sunlight from diffused matter extending in the form of a flattened disc beyond the earth's orbit. Prof. Seeliger, who attempted to explain the movement of the apse of Mercury by the attraction of this matter, assumed that nine-tenths of its mass was concentrated in a flat spheroid inside Mercury's orbit. Further, that the equatorial plane of this spheroid was nearly in the plane of Mercury. This is necessary in order to secure other elements of the orbits of the inner planets, such as the node of Mercury, from being disturbed. The arbitrariness of the assumption is evident.

(5) The slight alteration of the inverse square law will give the required movement to the apse of Mercury, and will not disturb any other planetary elements. It is a quite arbitrary assumption. (Further, it should be stated that the assumption is negatived by the movement of the moon's apse. Here a shift of 135″ would be produced. E. W. Brown's discussion shows no such excess of motion.)

Prof. A. FOWLER: It is generally known that Einstein's theory predicts a shift of the Fraunhofer lines towards the red by amounts equal to those which would be given by a radial velocity of 0·634 kilom. per second. In order to eliminate displacements which might arise from possible difference of pressure between the sun's reversing layer and the arc comparison, observers have given special attention to the lines composing the band of cyanogen λ 3883, which is free from pressure effect. In this region the theoretical displacement is 0·008 A.

Since radial convection currents would produce no displacement at the sun's limb, observations have been made at the limb as well as at the centre of the disc, the sun's rotation being eliminated by restricting observations to the vicinity of the sun's poles. Account has to be taken also of the slight general increase in the wave-lengths of the Fraunhofer lines in passing from centre to limb, which is called the "limb effect."

The actual observations may be summarised as follows:—

Observer.	Dispersion (mm. per A.).	Centre.		Limb.		Means.	
		Weaker lines.	Stronger lines.	Weaker lines.	Stronger lines.	Centre.	Limb.
Evershed, 1914	1·2–1·8	—	—	—	—	+0·005 (11)	+0·008
Schwarzschild, 1914	1·15	+0·0022 (21)	+0·0045 (13)	+0·0046	+0·0026	+0·0029	+0·0038
St. John, 1917	1·8–2·8	−0·0009 (25)	+0·0013 (18)	0·0000 (17)	+0·0036 (18)	+0·0002	+0·0018
Evershed, 1918	1·2–2·6	—	—	—	—	+0·004 (30)	+0·006
Grebe and Bachem 1919	1·0	—	—	—	—	+0·004 (36)	+0·004
				Mean	....	+0·003	+0·004

Evershed's first value has been omitted in forming the general mean, and in the case of Schwarzschild the limb displacements have been taken as the means of his values at distances of 0·93 and 0·97 of the sun's radius from the centre of the disc. The numbers in brackets indicate the numbers of lines measured.

If we could accept St. John's view that the greatest weight should be given to the weaker lines, and that there is practically no displacement either at the edge or at the centre, I think we should conclude, without hesitation, that the predicted Relativity effect does not exist. It would be too much to suppose that there could be two equal compensating effects, one at the centre and one at the limb, of totally different origin. If we take the general mean, we have a displacement at the centre of +0·003 in place of +0·008, and if the relativity effect exists we have to account for a compensating effect of 0·005 to the violet. This might conceivably be explained by an ascending motion of the solar gases with a corresponding velocity; but there must be descending as well as ascending gas, and it seems more likely that the descending gas would contribute to the absorption in greater degree than the ascending gas, so that the requisite compensation does not seem probable. At the limb, a compensating displacement of 0·004 towards the violet would be required; that is, a "limb effect" opposite in direction to that found for the metallic lines.

If the Einstein effect be supposed absent, a more probable explanation of the mean results can be given. At the centre we should merely have to suppose that the predominant absorption was given by the descending gas, giving a red displacement of 0·003; and at the limb we should have to assume a limb effect of 0·004 to the red, in accordance with the effect observed in other cases. Different interpretations may possibly be put on the observations, but my own opinion is that they are decidedly unfavourable to the existence of the Einstein effect.

Mr. E. CUNNINGHAM: In Einstein's prevision of an observable shift of the solar spectrum two distinct hypotheses are involved: the hypothesis of *Relativity*, and that of *Equivalence*. If we take the illustration of two identical atoms, A, B, at a distance apart in a field free from gravitation, the arrival at B of the waves from A must synchronize with the vibrations of B. If a gravitational field be simulated by viewing these atoms in a frame of reference in which they have an accelerated motion, the principle of Relativity requires that this synchronism shall not be broken, since a coincidence of two events in time and space may never be resolved into non-coincidence. But the principle of Equivalence has nothing to say in this case. It only comes into play when we compare the action of an atom in a simulated gravitational field with its behaviour in a real gravitational field which, not being susceptible of being transformed right away, is associated with the presence of matter. Then, inasmuch as a real gravitational field may be simulated as far as the values of g_{rs} and their first differential coefficients are concerned, if the behaviour of the atom depends on these only we may, I think, admit Einstein's hypothesis that ds as the measure of the "interval" between the emission of two successive pulses is the same for a given atom in all fields. But in the case of the real field it appears that the mode of transmission through the ether will not be such as to disguise the consequent change of period. Here then appears to be a real difference between a real gravitational field and a simulated field.

The early restricted principle of Relativity was blamed by some physicists for taking away their ether. Does the generalisation make the situation worse, or does it clear the way for an attempt at reconstruction? The criterion for any conception of an objective ether is that the specification of it must be by means of invariant relations. A definite velocity must be assigned to any element of it which transforms in any change of the space-time framework in the same way that the velocity of any material element transforms. It is certain that a revision and completion of the customary specification of stress, momentum, energy, and flow of energy requires a velocity to be attributed to the medium in which these exist, in order that the stress may account exactly not only for the flux of momentum but for the flux of energy as suggested by Poynting. Analysis shows that along these lines an objective moving ether may be conceived which is consistent with the requirements of the Relativity theory.

Prof. H. F. Newall: Einstein has said that the merit of theories of principle is their logical perfection and the security of their foundations. We are here dealing with a theory of principle. We have to be very sure of the foundations before we accept it. When one thinks of Fitzgerald's guess about the celebrated interference experiments, it is difficult to conceive that two different substances, like Michelson and Morley's sandstone slab and Morley and Miller's pinewood planks, should make such a beautiful adjustment of a contraction in length to a compensating expansion in time.

I wish to put a point to Mr. Jeans, relating to the central conception, which he has referred to as difficult to grasp. Observers S and S′ are in stationary ether at the origin when a flash of light is emitted from it; S remains there, S′ moves along a radius. White diffusers are distributed all over a sphere, of radius say 100 light-seconds, round the origin. Then after 200 seconds S will see all the diffusers flash simultaneously. My question is: Is it now maintained that S′ will not see the fore diffusers flash first, the lateral diffusers take it up next, and the aft diffusers flash last? If we superpose a uniform ether-wind in any direction, we get back to the general statement of the Michelson-Morley experiment in terms of an instantaneous flash instead of continuous illumination.

I have some remarks to make about refraction—a subject which will take me seven minutes to set forth. Perhaps it will be better to refrain at this late hour.

Mr. Jeans: As regards Prof. Newall's problem, it is not maintained that the flashes would be seen simultaneously by S′—he would not expect them to be, because the material surface which appears to be a sphere at rest to S would appear to be something quite different to S′.

Prof. F. A. Lindemann: The assumption that an atom is not changed by being brought into a gravitational field seems doubtful. Its frequency $\nu = \frac{2\pi^2 E^2 e^2 m}{h^3}$ times some pure number. m increases on account of the radial contraction exactly enough to balance the Einstein effect, unless this increase in its turn is compensated by a change in E^2 and e^2. If so, the spectral shift would be required by the definition of ds. If not, its absence, if it really is absent, would be explained.

Whether the fact that Einstein's theory contains the principles of the conservation of energy and momentum is in its favour, seems doubtful, since they are derived by using Hamilton's principle which notoriously fails in the ultimate processes of atomic interaction.

Relativity, however, appears to favour the undulatory view of the propagation of radiation as opposed to light-quanta. If these existed they would have a finite mass due to their electric field for an observer moving with them. This mass should vary with the velocity as that of an electron, and become infinite for any other observer. Incidentally, Relativity deprives us of evidence for the assumption that an electron's mass is electromagnetic. Any mass would vary in exactly the same way.

I regret the tendency to emphasize the metaphysical rather than the physical interpretation of Einstein's equations. Thus the statement that a sphere of water of radius $5{,}7 \cdot 10^{13}$ cm. would occupy all space appears to me wrong. That an observer on such a sphere would believe it to occupy all space I agree, but we are not bound to accept his conclusions.

Dr. L. SILBERSTEIN : In view of the late hour but two brief remarks : *Firstly*, the attempt at connecting the spectrum-shift question with the quantum theory cannot help very much. As I have shown at the last meeting of the Royal Astronomical Society, the predicted shift cannot thus be compensated without artificiality. And as to the effect itself, Einstein himself considers it as theoretically unavoidable, and so do the leading Continental physicists, among whom W. Wien, who agrees with me that it is premature to see in the Eclipse results a confirmation of Einstein's theory. *Secondly*, and at the risk of committing what nowadays may seem a heresy, I should like to draw attention to the possibilities offered by Stokes-Planck's ether which seems to acquire vitality exactly due to the change of light-velocity around the sun observed by the astronomers. Details are given in my paper in the 'Philosophical Magazine' for February. In this connection also a certain crucial first order (v/c) experiment suggests itself, which I hope to elucidate at a later opportunity.

On the Viscosity of Sulphur.

By C. Coleridge Farr, D.Sc., F.P.S.L., Professor of Physics, and D. B. Macleod, M.A., B.Sc., Lecturer in Physics at Canterbury College, University of New Zealand.

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Historical.

A great amount of work has been done on the composition and properties of liquid sulphur by Prof. Alexander Smith and his collaborators, mainly at the University of Chicago.

The general conclusions arrived at by them may be briefly stated as follows: Ordinary liquid S consists of two modifications of sulphur known as S_λ and S_μ, of which S_λ is very soluble in CS_2, whereas S_μ is practically insoluble. The percentage composition of S_λ and S_μ in liquid S varies with the temperature, but provided the temperature has been kept constant for a sufficient length of time the percentage composition at any particular temperature is always the same, though various impurities such as SO_2, NH_3, H_2SO_4 may retard or accelerate the attainment of a state of equilibrium. The percentages of S_μ, when equilibrium has been attained, have been given by Smith and Holmes* and Carson† on a continuous curve from 120° C. to 440° C., and from this curve it seems that the S_μ varies from 3·75 per cent. at 120° C. to 34 per cent. at 440° C. A sharp rise in the percentage of S_μ takes place at about 160° C., corresponding with the increased viscosity of S about that temperature. An apparent exception to the general rule for impurities was found for iodine with which higher percentages of S_μ were obtained. Smith and his collaborators do not claim that the percentages given by them are the actual percentages in liquid S, as in the process of chilling some S_μ may revert to S_λ, and thus the percentage of S_μ may be too low. By chilling a stream of burning S they found a percentage of 51 per cent., which would seem to indicate that the value 34 per cent. at the boiling point as found by ordinary chilling was too low.

In this work on sulphur, though the viscosity is referred to, no exact measurements have been made, and only the temperature at which obvious thickening has taken place is referred to.

Not a very great amount of work has been done on the viscosity, though it has long been known to be anomalous. A résumé of work done prior to 1905 is given by Rotinjanz in his paper on the changes in the viscosity of liquid sulphur,* but no results which are certain in their value have been obtained. Rotinjanz tested the viscosity by a modification of Ostwald's viscosimeter, and examined it from the melting point to the boiling point. All his experiments, however, seem to have been carried out with rather rapidly rising or falling temperatures, so that a state of equilibrium in the S, or even a state of uniform temperature could not be secured. His temperatures rose at rates varying from 0·27° C. to 2° C. per minute. His main results were that with moderate rates of heating (0·27° to 1° a minute) the sulphur reached a maximum of viscosity (52,000 relative to water) at 187° C., while with greater rates of rise of temperature the maximum of viscosity occurred at higher temperatures. On cooling S from temperatures above 230° C. the maximum viscosity was lower and the temperature at which it took place higher than with rising temperatures. He also found that the higher the temperature to which the S had been heated before the gradual cooling began the lower was the value of the maximum viscosity on the downward grade, and the higher the temperature at which it occurred.

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* Smith and Holmes, 'Z. Physik. Chem.,' vol. 54, p. 257 (1905).

† Carson, 'J. Amer. Chem. Soc.,' vol. 29, p. 499 (1909).

Rotinjanz also states that S, through which NH_3 has been passed, has a maximum viscosity relative to water of 19,000 at 180° C., and he draws the conclusion that there is no connection between the viscosity and the percentage of S_{μ}.

We have been unable to find any later work on the viscosity of sulphur.

Method of Experiment.

On account of the great viscosity of S from 170° C. to 220° C., we found Ostwald's viscosimeter method unsuitable for determinations at these temperatures, though well suited to temperatures up to 160° C. We decided, therefore, to adopt the method of rotating cylinders for our determinations. Our method was as follows: A glass tube, D (fig. 1), sealed at one end, contained a thermometer, C, reading to 360° C., and sufficient mercury to give stability to the system, and also to enable the thermometer to take up its proper temperature quickly. This tube had an external diameter of about 1·4 cm., and the system weighed about 150 grm. This was suspended by a bifilar system, BB, passing over a small light pulley, A, and through two fine holes, FF, GG, is a small piece of iron, in which are fine holes at different distances from the central one, and the suspension wires passing through two of these would immediately be at a known distance apart at the bottom. This small plate of iron was slipped into a cap fitted on to the tube D. The small pulley, A, enabled the system to take up a vertical position without further adjustment, and also secured the equal tension on each thread of the suspension. When measuring viscosity in sulphur, the length of the suspension was about 16 cm. and the width about 6·5 cm. Fine copper wire (0·019 cm. diameter) was used for the suspension. The tube D was lowered into a larger outer test-tube, E, of good cylindrical form, the internal diameter of which varied in the different measurements

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* 'Zeit. Physikal. Chem.,' vol. 62, pp. 609–621 (1908).

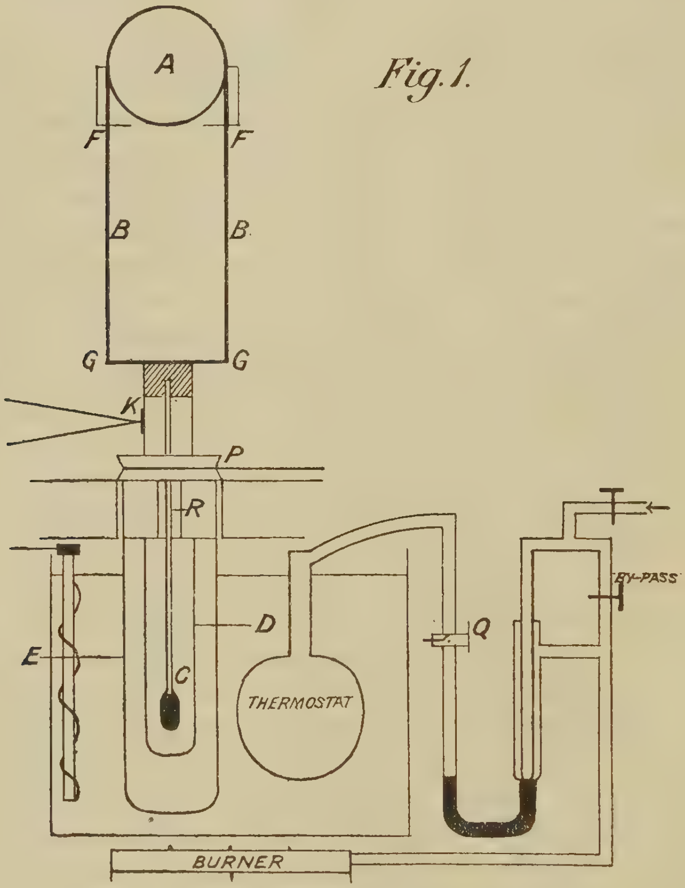

Fig. 1.

from 3 cm. to 3·5 cm. This test-tube contained the sulphur to be examined, and could be rotated by means of a pulley, P, at any desired speed. The pulley and system, into which the test-tube was packed with asbestos, rotated on a fixed stand, L, care being taken that the test-tube was vertical after being packed. A mirror, K, was attached to the tube, D, and the deflection was measured by the movement of the spot of light reflected from this mirror from a lamp on to a circular scale. In all later experiments a paraffin bath was used, to give a temperature up to 220° C., the paraffin being vigorously stirred and the temperature governed by an air regulator. By means of a three-way tap at Q, any temperature desired could be quickly reached, and then maintained constant. By means of a window, R, in the framework holding the tube, E, the temperature of the thermometer, C, could be read and compared with the temperature of the bath. This was most important, as it was found that, on account of the poor conductivity of sulphur, it took as long as three-quarters of an hour for the two temperatures to become the same.

By altering the length of the suspension and the distance apart of the wires, any degree of sensitiveness could be obtained. For sulphur below a temperature of 160° C., a unifilar suspension was used, consisting of copper wire (0·019 cm. diameter), of length about 60 cm. With this arrangement the system was very sensitive (though, of course, it could have been made much more so), and had to be protected from air currents by a glass covering. The bifilar system was very stable, and took up its final deflection rapidly, and without much movement of the spot.

The expressions used to calculate the viscosity were the usual ones used for bifilar and unifilar suspensions, and for the rotating cylinder method, viz., for the bifilar

$$\eta = \frac{(a-b)(a+b)\,mgd_1d_2}{16\pi a^2b^2\omega hl}\,.\sin\theta,$$

where b = radius of inner cylinder.
a radius of outer cylinder.
m mass of suspended system in grammes (less amount due to displacement of S).
d_1 and d_2 width of suspension at top and bottom.
ω angular velocity of rotation of E.
h depth of immersion of tube D in sulphur.
l length of suspension.
θ angle of deflection.

The speed of rotation was taken with a stop-watch, and was generally of the order of one revolution in about five seconds. By means of lamp resistances and a motor with a magnetic brake the speed could be easily varied, and as a check the deflections at three or four different speeds were always taken.

For the unifilar suspension the expression used was

$$\eta = \frac{\pi l_1 m_1 (a_1^2+b_1^2)(a-b)(a+b)}{12\,l\,T^2a^2b^2\omega h}\,.\,\theta,$$

where T is the time of oscillation of a rectangular bar of mass m_1, about an axis perpendicular to its dimensions (sides), a_1 and b_1, and suspended by a wire of length l_1, which is the same wire as was used in the experiment.

These expressions were tested with glycerine and water, and gave good agreement with their known values. With reasonable care all the quantities could be measured within 1 per cent. of error.

We have found, like most other workers with sulphur, great difficulty in securing consistency in our results. An important part of this paper will be a discussion of these inconsistencies. On account of the enormous variations in the values of the viscosity of S at different temperatures, and also, as we shall show, with different samples at the same temperature, the viscosity of sulphur provides a far more sensitive method of noting changes in S than any other of its physical properties, such as density, coefficient of expansion, or surface tension.

In our early experiments the viscosity was studied with ascending and descending temperatures. By means of a mercury bath, temperatures up to 300° C. were obtained, though most of our work was done below 230° C., the highest temperature to which a paraffin bath could be taken with safety. Fig. 2 gives the general results obtained by this method. Curve I represents the viscosity curve of a sample of twice distilled S which had been collected in the ordinary way and allowed to crystallise. Curve I was taken with ascending temperatures, and the highest temperature reached was about 278° C. After reaching this temperature, the temperature was gradually decreased and readings taken (after seeing that the thermometer in the bath and that in the tube D read the same) at the same temperatures on the down grade as they had been on the up grade. In addition to these, special readings were taken at the maximum on both the up and down grades. The values of the viscosity with falling temperatures are shown in curve II as they are with rising temperatures in curve I. Curves III and IV give the values after allowing the sulphur to remain heated to 150° C. during the night, curve III with ascending temperatures, and curve IV with descending. The values of the viscosity in these curves are given in arbitrary units only, though all later values are given in C.G.S. units. Two things are to be noticed from these curves: (*a*) the marked lowering of the viscosity with descending temperatures, thus confirming the results of Rotinjanz (*loc. cit.*) (As was also pointed out by him, the lower the maximum value of the viscosity the higher the temperature at which it occurs), and (*b*) the marked effect of keeping the S at a temperature of 150° C. for 18 hours.

A series of experiments was next made with a view to connecting, if possible, the amount of S_μ present in the S with the viscosity. Test-tubes containing some of the same sample of S as was being used for the viscosity test (as a general rule twice distilled S) were placed in the bath along with the viscosity tube, and as the tests for viscosity were made at various temperatures a small test-tube was withdrawn and plunged into ice. This small test-tube had a smaller rod of glass within it, in order to confine the S to be analysed for S_μ to a film on the outside, so that it might all quickly cool. The analysis was done in the same way as by Smith and Holmes.*

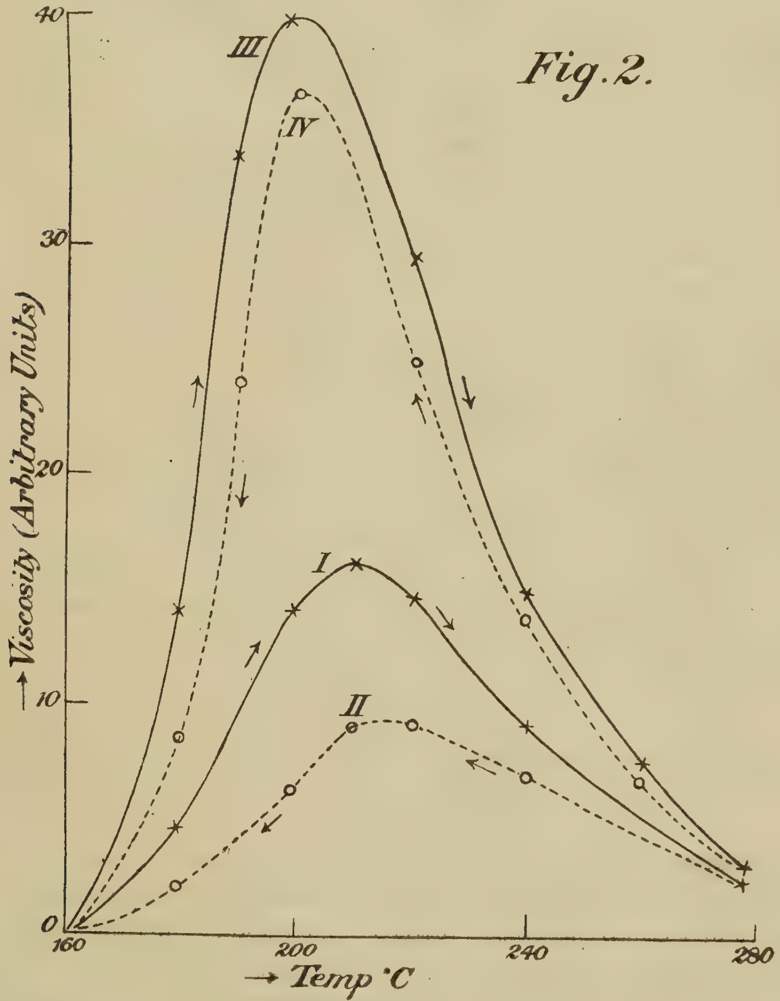
Fig. 2.

The temperature was kept constant till the thermometer in the bath and that in the tube D read the same.

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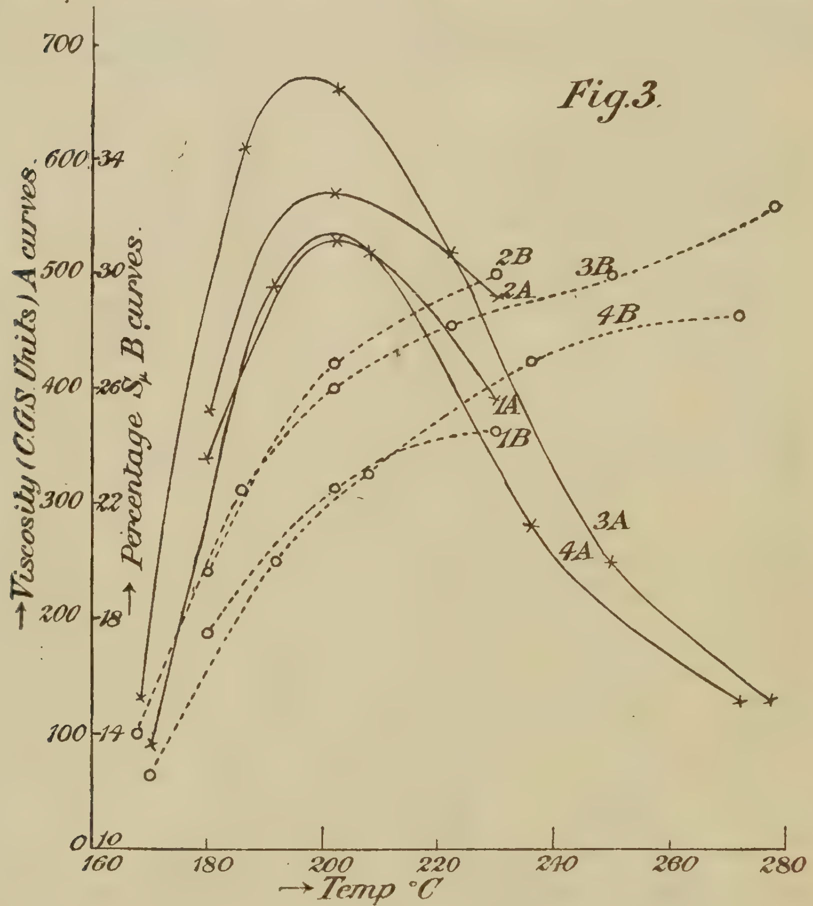
* 'J. Amer. Chem. Soc.,' vol. 27, No. 8 (1905).

The results from this set of experiments are illustrated in fig. 3, the individual experiments being marked 1, 2, 3, and 4.



The experiments illustrated in the curves marked 1 and 2 were taken with the same sample of sulphur, but curve 2 after a greater period of heating. Curves 3 and 4 refer to samples different from 1 and 2 and from each other. The corresponding curves for viscosity and S_μ are marked A and B respectively. Thus 2 A is the viscosity curve corresponding to the S_μ curve 2 B. These curves indicate that different samples have different percentages of S_μ, and also that the higher the percentage of S_μ present the greater the viscosity at any particular temperature. In this respect curve 2 is not in such good agreement with curve 3 as the other samples.

A series of measurements, using the unifilar suspension, was next made at temperatures below 160° C. Consistent results were obtained at these temperatures, though we have not examined the viscosity under such varied conditions as at higher temperatures. A sample of twice-distilled sulphur was maintained at a temperature of 135° C. during the night and tested the following day. The deflection given is a mean of eight or ten different readings at each of several different speeds, as the unifilar deflection was not so steady as the bifilar. The values of the deflection at the different speeds of rotation were reduced to the same speed, and the agreement between the observations was then very good. Other samples of twice-distilled sulphur gave similar values.

Temperature.	Viscosity in C.G.S. units.	Deflection in mm.
° C.		
123·0	0·1094	111
135·5	0·0866	88
149·5	0·0709	72
156·3	0·0719	73
158·2	0·0759	77

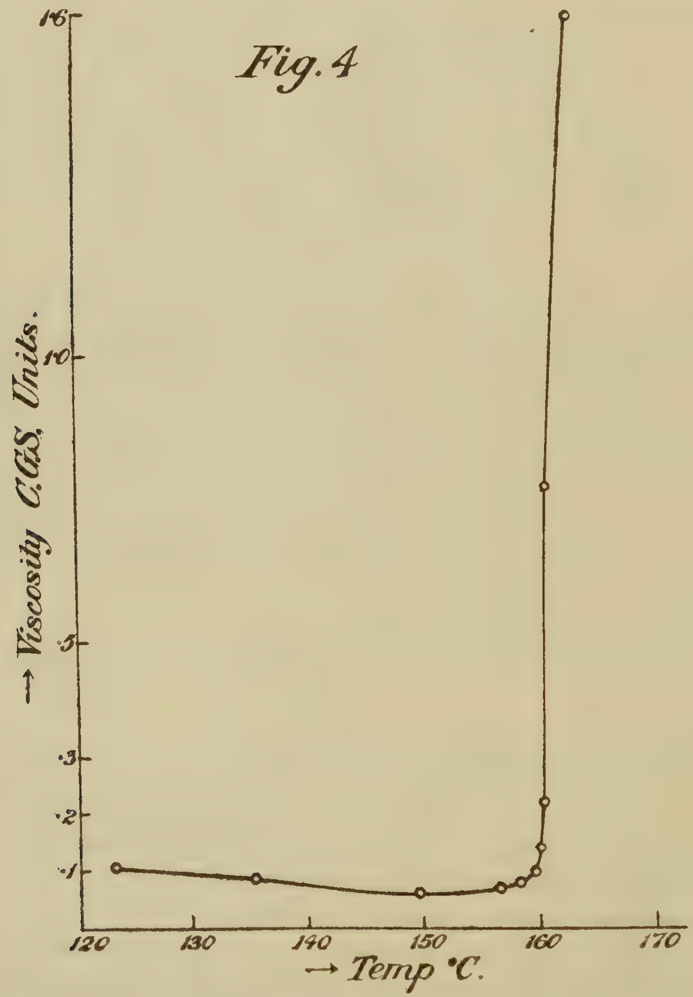
These figures indicate a minimum viscosity in the vicinity of 150° C. An undoubted increase had taken place at 158·2° C. On raising the temperature to 160·5° C. the deflection became too great for the system, indicating a decided increase between 158·2° C. and 160·5° C. As far as we have at present investigated it, the change in viscosity in the neighbourhood of 160° C. is not of the nature of a sharp and abrupt change, but a gradual bending round, and can be traced back at least as far as 158° C. Though we have not yet made a special series of experiments at 160° C., the following were observed at temperatures from 159·2° to 160·3° C.:—

Temperature.	Viscosity.	Temperature.	Viscosity.
° C.			
159·2	0·0948	160·0	0·2283
159·5	0·1445	160·3	0·7732

A later experiment, in which the minimum was especially sought, confirmed the statement that a definite increase had taken place at 158·2° C. above that at 152° C., and also that the change from 158·2 C. to 160° C. was gradual, and that over this small range of temperature the change is elastic (it is not so over great ranges of temperature), and that lowering the temperature reproduced the results obtained on the upward grade. To show the character of the changes observed, the following deflections, which were the mean in each case of 40 oscillations, may be quoted:—

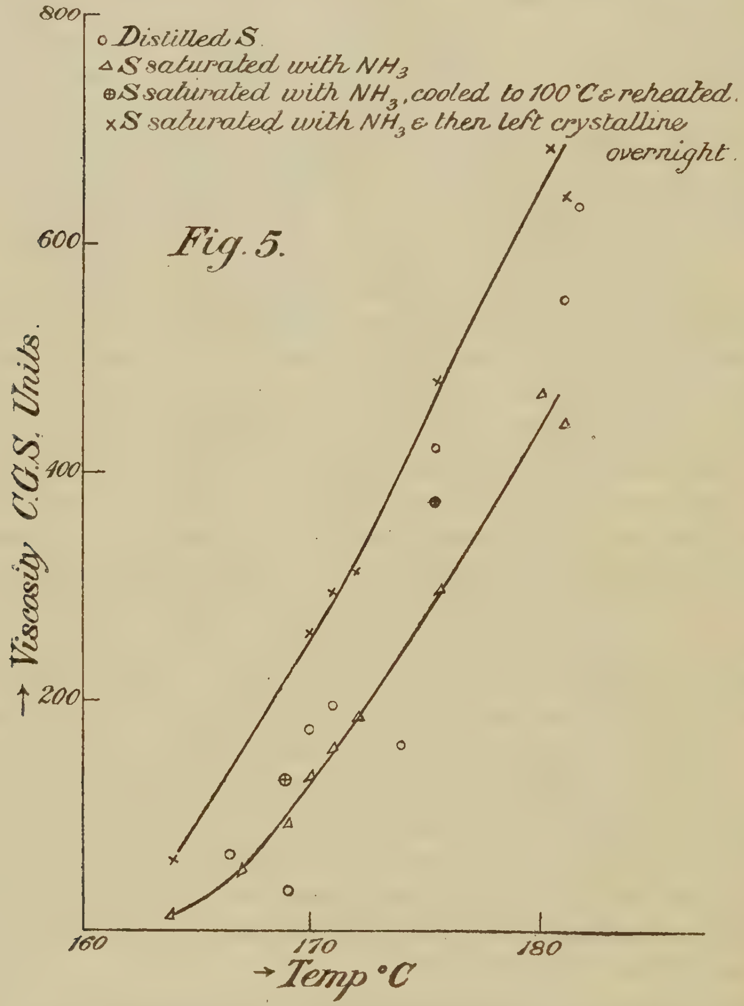
Temperature.	Deflection.	Temperature.	Deflection.
° C.		° C.	
140 ·0	116 ·5	158 ·5	112 ·8
152 ·0	100 ·0	159 ·4	212 ·0
158 ·3	108 ·8		

Fig. 4 gives a graphical representation of the changes to 163° C. We consider that the evidence of the viscosity is that there is not a transition point in the strict sense of the word in the neighbourhood of 160° C., though the viscosity undergoes a marked increase in the range of a few degrees from 159° C. to 163° C.



It is in the range of temperature from 160° C. to 230° C. that we have found the most marked variations in the values of the viscosity of different samples of sulphur of seemingly equal purity, when the viscosities of those samples were compared at the same temperature within this range, and it is here consequently that most of our work has been so far done. In view of the work of Smith and his collaborators, and their opinion that sulphur through which NH_3 had been passed takes up an equilibrium value between S_λ and S_μ ($S_\lambda \leftrightarrows S_\mu$) rapidly, we had hoped to obtain a consistent sample by ammoniating twice-distilled sulphur. It was very soon noticed, however, that the amount of NH_3 absorbed had a great effect upon the viscosity of the S. Sulphur has the power of absorbing great quantities of gas especially NH_3 and SO_2, and on passing either of these gases through molten S at 150° C. for several minutes and then allowing the sulphur to crystallise, large quantities of gas were given off, so much so that a large blob was formed at the surface of the sulphur at the time of crystallisation due to the gas forced out of solution by this act. Notwithstanding this, further considerable quantities are evolved on remelting. We have found as the result of many repeated experiments that sulphur through which NH_3 has been passed for several minutes gave over the range 160° C. to 180° C. a fairly "low" valued viscosity curve, but on allowing the sulphur to crystallise, and consequently rid itself of considerable quantities of dissolved gas, the viscosity value at any temperature invariably rose, giving what we term a "high" curve. It was observed that S saturated with ammonia at 150° C. tended to give off the gas between 170° C. and 180° C., but on account of the great viscosity, the gas was not able to escape from the mass. The experiments illustrated by fig. 5 show that irrespective of the value of the viscosity of the S used, samples saturated with NH_3 give consistent values, and also samples from which a certain amount of the gas has been driven out by crystallisation. On remelting, intermediate values are obtained when the sulphur had been crystallised but not allowed to cool.

In fig. 5 the viscosities at different temperatures of the original four samples of twice-distilled S are marked with a circle. On saturation with ammonia at 150° C. and then determining the viscosities at different temperatures the different values obtained are marked with a triangle. On crystallising but not allowing to cool below about 119° C. (the melting point), then rewarming and redetermining viscosities, the values obtained are marked with a cross enclosed in a circle. Finally crystallisation, cooling to ordinary temperatures by allowing the sulphur to remain all night in the crystalline form, and then reheating and determining viscosities again next day, gave the different values marked with the cross. It will be seen that a quite satisfactory curve will pass (*a*) through the triangles, and (*b*) through the crosses, whilst the values obtained from the other two methods of procedure are irregularly distributed about. Smith and Holmes (*loc. cit.*) argue from the behaviour of ammoniated S that the percentage of S_μ in ammoniated sulphur is the same as in ordinary sulphur, but the experiments do not support the view that the viscosity is a function of the amount of S_μ present. It is possible that large quantities of dissolved gas may reduce the viscosity by simple mechanical means.



A similar experiment with SO_2 instead of ammonia gave a lower value with excess of SO_2 than when it had been allowed to crystallise out.

These results show that the viscosity of sulphur treated with either NH_3 or SO_2 depends largely on the amount of these gases present. We are, however, leaving the whole question of the effect of dissolved gases for a later paper.

Temperature.	Viscosity.	Remarks.
° C.		
171 ·0	181 ·5	Twice-distilled sulphur.
171 ·0	161 ·0	Sulphur saturated with SO_2 at 150° C. and then reheated.
171 ·0	185 ·0	Sulphur allowed to crystallise and then reheated.

With ordinary twice-distilled sulphur the results were irregular. It was, however, found that if the sulphur were distilled and somewhat rapidly cooled, so that it became solid soon after flowing into the receiving flask, and so that there was no great quantity in the liquid form in the receiving flask, a low viscosity curve was obtained. On the other hand if the sulphur was distilled so rapidly that it remained liquid in the receiving flask until the operation of distillation was completed, a somewhat high valued viscosity curve resulted. Moreover, on keeping a low or medium valued sulphur at any temperature from 120° C. to 160° C. for a length of time, the viscosity, as measured at some temperature between 160° C. and 190° C. (the viscosity was generally measured at about 171° C.), invariably rose, finally reaching a maximum. This change was a slow one, in some cases as much as 36 hours elapsed before the viscosity reached its final value, and it always required some 18 or 20 hours. Also repeated crystallisations had the effect of slowly raising the viscosity of a low sample. As has been found also by Rotinjanz, if a sample of comparatively high valued viscosity were heated to 230° C. or higher and then recooled to 170° C. its viscosity was diminished.

In illustration of these results the following experiments may be quoted: In these experiments the viscosity was tested at 171° C., though occasionally the temperature was raised to 180° C., and again lowered at 171° without appreciable change in the viscosity. The effect of crystallisation is shown by the following typical experiment:—

Temperature at which the viscosity was measured.	Viscosity.	Remarks.
° C.		
171 ·0	100	Twice-distilled sulphur.
171 ·0	121	The sulphur was then allowed to remain crystalline all night.
171 ·0	141	Crystallised through night as before.
171 ·0	164	Crystalline over week end.
171 ·0	176	Crystalline over night.

No gradual increase (proportional to time) nor other effect was observed owing to the sulphur remaining long in the solid state, as two samples, one giving a low value and the other a high, were left in their tubes for four weeks, but, on retesting, gave similar values to their previous ones, the lower one only having risen by the amount due to a single crystallisation, and the higher one remaining constant.

The following experiment shows the combined effect of crystallisation and of keeping the sulphur for stated lengths of time at a temperature of 125° C. The temperature at which the viscosity was measured was 171° C. throughout:—

Viscosity.	Remarks.
57·2	Twice-distilled S, quickly cooled.
90·4	Kept 3 hours at 125° C.
102·4	Crystallised throughout night.
133·0	3 hours at 125° C.
143·3	Crystallised during night.
187·5	4 hours at 125° C.
196·8	Crystallised through night.
242·0	4 hours at 125° C.
247·3	Crystallised during night.
284·6	3 hours at 125° C.
284·6	Crystallised through night.
336·3	3 hours at 125° C.
336·5	Crystallised through night.
368·5	4 hours at 125° C.
347·0	Crystallised through night.
375·1	4 hours at 125° C.
425·7	All night at 125° C.

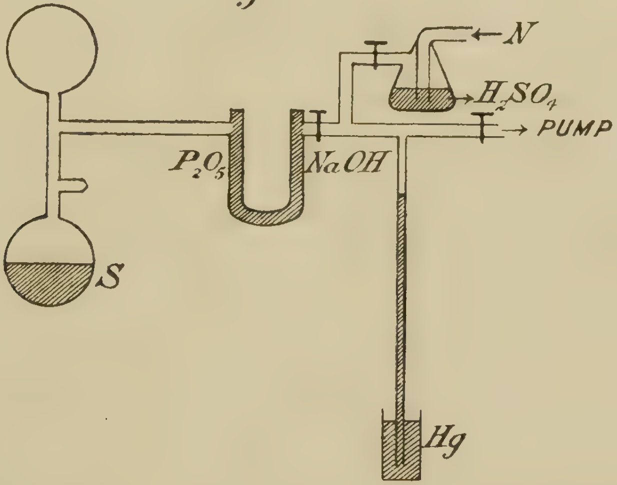
It will be noticed that, while the sample has a low viscosity, crystallisation seems to raise it. This may possibly be partly or wholly due to the fact that in order to crystallise, the sulphur has to cool down somewhat slowly from 171° C. (the testing temperature) to the solidifying point, and then next day has been rewarmed through the same range of temperature, during which there would be an increase in accordance with the proved effect of keeping it in the limpid condition. But while this may be so, it is difficult similarly to explain the slight lowering effect which crystallisation certainly seems to have on a high valued sample.

A similar experiment in which the temperature was 141° C. instead of 125° C. gave similar results, though the viscosity rose more rapidly. After 22 hours' heating in three and four-hour periods the viscosity rose from 80·7 at 171° C. to 393 at the same temperature, and after then remaining all night at 141° C., it rose still further to 466 at the same testing temperature. Two consecutive crystallisations reduced this to 440, but on again heating it all night at 141° C. it rose to 470 (tested at 171° C.) which, therefore, seems to be a maximum for that temperature. A similar maximum had been obtained on another occasion after prolonged heating.

On then passing ammonia into this high valued sample (470) its viscosity fell to 282 (as measured at 171° C.), but rose again to 326 on allowing the sulphur to just crystallise and then reheating to the testing temperature, thus confirming in a general way the previous values with NH_3.

With a view to tracing the cause of these changes a series of experiments was made in which the sulphur was heated in a vacuum and under nitrogen. Three experiments were made in which the sulphur was placed in a vessel consisting of two distilling flasks fused together as in fig. 6. The sulphur was drawn into the flasks in a molten condition, and the lower leading tube was then sealed off. The other was connected to a motor-driven oil vacuum pump capable of exhausting down to about 3 mm. or less, and also through drying tubes of P_2O_5, NaOH, and H_2SO_4 to a reservoir containing carefully prepared nitrogen. The sulphur in the lower flask was then melted under a vacuum and kept for some time at a low temperature under this vacuum, until at any rate all the visible bubbles of dissolved gas had been pumped out. The temperature was then allowed to rise, and as it rose N was admitted until the sulphur finally boiled under N at atmospheric pressure. The temperature was several times lowered to allow the flask to be evacuated again, and N was then reintroduced and the boiling repeated. The flasks were finally sealed off and one-half of the sulphur was decanted *in vacuo* into the upper flask, and there allowed to crystallise. The sulphur at the other end was kept at a temperature of about 140° C., or 150° C. for several days in an electric oven, out of which the crystallised half protruded and was thus kept cool. The viscosity of the two samples was then tested at

Fig. 6.



171° C. The viscosities in C.G.S. units in the case of two such sets of experiments A and B were as follows:—

	Portion kept crystalline.	Portion kept liquid at 150° C.	Remarks.
Experiment A ...	128	65	Kept at 150° C. for 24 hours.
Experiment B ...	251	182	Kept at 150° C. for 4 days.

The samples used in Experiment B were then exposed for 24 hours at a temperature of 150° C. to air, and then again tested for viscosity at 171° C., with the result that the viscosity of the portion which had been previously kept crystalline rose to 489, whilst that of the other was 484, and that of a third portion, kept for 24 hours in a semi-viscous state, at a higher temperature than 150° C., only rose to 396.

In a third experiment with the two flasks, the upper flask (the empty one) was thoroughly heated before decanting, with a view to driving off any impurity, such as H_2SO_4, that might have condensed there before decanting half the sulphur from the other end into it. In this case, the viscosity of the crystalline portion gave, at 171° C., a lower value (131) than that of the liquid portion.

On a drop of H_2SO_4 being added to the portion which had been kept liquid, without any special effort being made to produce complete diffusion, the viscosity (always tested at 171° C.) rose immediately to 222 C.G.S. units.

To test this question further, the previously crystalline portion (viscosity 131) was transferred to a smaller distilling flask, and again heated under a vacuum, and boiled under nitrogen, special care being taken to heat most thoroughly the upper part of the flask during the evacuations, in order to drive off any H_2SO_4 which might possibly have condensed there. By this process, the viscosity was reduced from 131 C.G.S. to 78 C.G.S., both measured at 171° C.

These experiments show that, whereas keeping sulphur exposed at a temperature of 150° C. to air, resulted in a rise of viscosity, in one instance from 182 C.G.S. to 484 C.G.S. in 24 hours, keeping it at 150° C. under a vacuum for five days resulted in the viscosity being actually lower than that of the sample of the identically same sulphur kept crystalline.

The results were still unsatisfactory, however, in that they failed again to give consistent results for the final values, presumably because they failed to remove the impurities present in the sulphur, such impurities as H_2SO_4 being able to condense in the cool upper flask.

With a view to preparing a sample of special purity without, however, going to the extreme precautions used by Threlfall and Brearley* (as we were rather seeking the effect of dissolved gases and their products than of such solid impurities as selenium and arsenic), commercial rolls of sulphur were first filtered hot, and then carefully distilled four times in very specially cleaned retorts and receivers, the first and last portion of each distillate being rejected. During the last distillation, the sulphur was rapidly cooled by allowing it to flow into a receiver kept floating in water, so that there was never more than a few cubic centimetres of it liquid in the receiver at any time. The final product presented a uniform colour, and had the appearance of purity, and in neither of the last two distillations were there any of the "black spots," which are so frequently mentioned by workers with sulphur, left in the retorts. We may say that we consider these black spots are "ordinary dirt" of almost any kind, which sulphur is very prone to take up and conceal. We think there can be no doubt that liquid sulphur is a very great solvent both of gases and solids. Two portions of this sulphur, which had been boiled under nitrogen for about an hour and sealed off under a vacuum, gave for viscosity at 171° C. the values 95 C.G.S. and 120 C.G.S. respectively. The second sample had been kept at 200° C. for about three hours and at 150° C. for 24 hours (both under a vacuum), but the difference of viscosity was probably due to the less vigorous boiling and heating of the upper portion of the flask. A third portion of the same sulphur was therefore taken, and submitted to a more vigorous boiling, heating, and evacuating. Before melting the sulphur in the small flask in which it was contained, the flask and solid sulphur in it were evacuated to a few millimetres of mercury twice, and each time purified nitrogen was admitted. It was then re-evacuated, and the sulphur was melted under a vacuum. As usual, a large volume of gas escaped. When no further gas appeared, the temperature was raised, and nitrogen allowed to pass in slowly, until the sulphur boiled at atmospheric pressure under nitrogen. The sulphur was kept boiling for 5½ hours, and the vessel in which it was contained was evacuated four times during the process. It was necessary for this purpose to allow the sulphur to cool to about 300° C. The upper part of the neck of the flask was frequently and vigorously heated, and the flask was finally pumped out to a few millimetres of mercury and sealed off. The sulphur, on being allowed to crystallise, presented a uniform appearance, but of a quite unusual character, the crystals being needle-like and of a transparent greenish colour, totally different from the original colour of the sulphur. This greenish appearance had been noticed before with sulphur which had been boiled for some time and allowed to crystallise *in vacuo*, and was at first thought to be due to an impurity, but, when later the flask was broken open, and a small portion of the melted sulphur recrystallised whilst exposed to air, it quite regained its original yellow appearance, showing that the greenish colour is due to the sulphur being gas-free. It is possible that these greenish crystals may approach pure monoclinic sulphur.*

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* 'Phil. Trans. R. S.,' A, vol. 187 (1896).

It happened that this purified evacuated sulphur was kept for 48 hours *in vacuo* before the flask was opened and the viscosity tested. During that period very small patches of the yellow opaque sulphur had begun to develop, but the change seemed slower than usual, and it is possible that, with still greater purity and a better vacuum, the greenish variety might not revert to the yellow. For the viscosity test the sulphur was remelted *in vacuo*, and quickly transferred to the testing tube in the bath, which had been adjusted to 171° C., and the test was made as soon as the thermometer within the inner tube had reached 171° C. Readings of the viscosity were also taken at the other temperatures given below. No diminution in the viscosity on the downward grade of temperature was observed after the temperature had risen to 220° C. and was being cooled again. We consider that these values of the viscosity are a near approach to the values for pure gas-free sulphur:—

Temperature.	Viscosity in C.G.S. units.	Temperature.	Viscosity in C.G.S. units.
° C.		° C.	
165·0	5·0	200·0	215·0
171·0	45·0	210·0	205·0
184·0	160·0	217·0	191·0
190·5	197·0	220·0	186·0
197·5	213·0		

This last experiment, together with the previous ones, shows conclusively that the presence of air is necessary for the production of a sample of sulphur with a very high viscosity curve, and, as some form of oxidation is undoubtedly the effect of exposure to air, SO_2 or H_2SO_4 are the substances most likely to be producing the effects.

SO_2 does not appear to be the chief disturbing impurity, because—

(1) Repeated crystallisation and remelting under a vacuum which would remove dissolved gases should show a marked effect on the viscosity, whereas these alone have proved to be incapable of reducing the viscosity of a high sample.

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* Though, as has been pointed out to us by Prof. Evans, experiments are needed to show that this greenish colour is not due to impurities derived from the glass, the colour of which alters on slight oxidation.

(2) Freshly distilled sulphur which invariably contains SO_2 gives both low and high values, the result depending apparently on the rapidity of cooling.

(3) Passing SO_2 into sulphur even to saturation has only a comparatively slight effect on the viscosity.

In favour of H_2SO_4 the following considerations may be adduced:—

(1) The impurity received on exposure is not removed below a temperature of about 220° C., about the temperature at which H_2SO_4 finally dissociates. The lower values of the viscosity on the descending temperature, observed by Rotinjanz and ourselves after a temperature of 220° C. has been reached, can be explained by the dissociation of the H_2SO_4 present in the S.

(2) The great difficulty in removing the impurity even with continued boiling suggests H_2SO_4, which would readily recondense in any cool portion of the flask.

(3) The low valued viscosity sample of sulphur which results from a rapid cooling to the solidification temperature may be explained by the H_2SO_4 not having had an opportunity to form in any quantity.

(4) The generally high value which results from allowing the sulphur to distil so quickly that the stream of molten sulphur flowing into the receiving flask keeps that already there in a melted condition throughout the whole operation—that is to say, at about a temperature of 150° C.—is on this view due to the exposure in thin extended layers of sulphur at a temperature of 150° C. to the oxidising effect of the atmosphere. Keeping a low or medium valued sample at a temperature within the very viscous range (160° C. to say 200° C.) does not in the same way increase the viscosity on account of the immobility of the particles.

(5) On distilling sulphur, or on boiling it in distilling flasks, small drops of a clear liquid, which could not have been water on account of the temperature, were frequently noticed in the cooler portion of the flask.

(6) Other workers* have shown that H_2SO_4 occurs in sulphur which has been exposed to air and have found it hard to remove.

(7) The effect of a drop of H_2SO_4 was to markedly increase the viscosity of a medium valued sample.

Thus, we incline to the view that sulphuric acid is largely responsible for the main increase of viscosity with exposure in a molten (but non-viscous) condition to the air, but while this is so we have shown that other impurities such as NH_3 and SO_2 have also an effect and that the effect seems to depend on the amount of impurity present. We differ, therefore, from Smith and his co-workers who consider that the effect of H_2SO_4, SO_2 and NH_3 is merely to retard or accelerate the attainment of a state of equilibrium which is finally independent of the nature of the impurity present. Each sample of sulphur behaves as a distinct sample giving a distinct curve, and the temperature could be raised 20° or 30° and allowed to fall again without any change taking place in the viscosity as measured at a fixed temperature (usually 171° C.) each time, proving as it appears to us that it was not a case of equilibrium merely.

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* Kellas, 'Jour. Chem. Soc.,' No. 674, p. 903 (1918).

Summary of Results.

(1) The viscosity of purified (twice distilled but not gas free) sulphur has a value at 123° C. of 0·1094 C.G.S. units. It falls to a minimum of 0·0709 at 150° C. and then gradually rises to about 159° C. when the rise becomes more marked, but nothing of the nature of a strict transition point is observed.

(2) Exposure to air in a molten condition, especially below 160° C., has a most marked effect on the viscosity from 160° C. onwards. The effect is a slow one, the viscosity continuing to rise (as measured at 171° C.) for as much as 48 hours on exposure for that time to the air.

(3) The maximum for purified unexposed (gas-free) sulphur is reached at about 200° C. and has a value of 215 C.G.S. units; the maximum for purified (not gas-free) sulphur, but after prolonged exposure to the air is reached at a lower temperature, viz., about 190° C., and can have a value as high as 800 C.G.S. units.

(4) Crystallisation has an apparent effect (though it may be a secondary effect) upon the viscosity as measured at any temperature. It apparently raises the viscosity (as measured at any temperature, say 171° C.) of a low valued sample of sulphur and lowers the viscosity of a high valued sample. The effect of crystallisation seems to disappear when the viscosity of the sample (as measured at 171° C.) is about 300 C.G.S. units.

(5) H_2SO_4 appears to be the chief impurity (formed from exposure to the air) which causes the extreme variations which are to be found in the values of the viscosity of air-exposed sulphur. Dissolved gases such as NH_3 and SO_2 also affect the viscosity.

(6) Evidence is adduced that the variations in the viscosity are accompanied by a corresponding variation in the amount of insoluble sulphur present.

We are continuing these investigations.

Our thanks are due to Mr. T. E. Kilworth for mechanical assistance in the manufacture of the apparatus.

On Kaufmann's Theory of the Impact of the Pianoforte Hammer.

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(Communicated by Dr. Gilbert T. Walker, C.S.I., Sc.D., F.R.S. Received November 7, 1919.)

1. *Introduction.*

The theory of the vibrations of the pianoforte string put forward by Kaufmann in a well-known paper* has figured prominently in recent discussions on the acoustics of this instrument.† It proceeds on lines radically different from those adopted by Helmholtz in his classical treatment of the subject.‡ While recognising that the elasticity of the pianoforte hammer is not a negligible factor, Kaufmann set out to simplify the mathematical analysis by ignoring its effect altogether, and treating the hammer as a particle possessing only inertia without spring. The motion of the string following the impact of the hammer is found from the initial conditions and from the functional solutions of the equation of wave-propagation on the string. On this basis he gave a rigorous treatment of two cases: (1) a particle impinging on a stretched string of infinite length, and (2) a particle impinging on the centre of a finite string, neither of which cases is of much interest from an acoustical point of view. The case of practical importance treated by him is that in which a particle impinges on the string near one end. For this case, he gave only an *approximate* theory from which the duration of contact, the motion of the point struck, and the form of the vibration-curves for various points of the string could be found.

There can be no doubt of the importance of Kaufmann's work, and it naturally becomes necessary to extend and revise his theory in various directions. In several respects, the theory awaits fuller development, especially as regards the harmonic analysis of the modes of vibration set up by impact, and the detailed discussion of the influence of the elasticity of the hammer and of varying velocities of impact. Apart from these points, the question arises whether the approximate method used by Kaufmann is sufficiently accurate for practical purposes, and whether it may be regarded as applicable when, as in the pianoforte, the point struck is distant one-eighth or one-ninth of the length of the string from one end. Kaufmann's treatment is practically based on the assumption that the part of the string between the end and the point struck remains straight as long as the hammer and string remain in contact. *Primâ facie,* it is clear that this assumption would introduce error when the part of the string under reference is an appreciable fraction of the whole. For the effect of the impact would obviously be to excite the vibrations of this portion of the string, which continue so long as the hammer is in contact, and would also influence the mode of vibration of the string as a whole when the hammer loses contact. A mathematical theory which is not subject to this error, and which is applicable for any position of the striking point, thus seems called for.

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* 'Annalen der Physik,' vol. 54 (1895).

† 'Proc. Phys. Soc.,' London, February, 1913; 'Nature,' 1913 and 1914, and 'Proc. Royal Institution,' 1914 (Prof. G. H. Bryan). See also D. C. Miller, 'Science of Musical Sounds,' Macmillan & Co., p. 207 (1915).

‡ 'Sensations of Tone,' English Translation by Ellis, p. 76, and Appendix V.

In the present communication, it will be shown how the general case of an inelastic particle impinging at *any* specified point on the string may be dealt with rigorously, and the magnitudes of the forces exerted during impact and the duration of contact may be calculated. To illustrate the method, a number of actual cases have been worked out numerically, and an attempt is made to compare the indications of theory with the results found in experiment.

2. *Analytical Theory.*

Two possible methods for dealing with the problem under consideration suggest themselves. The first is the rigorous application of the functional solutions of the equation of wave propagation after the manner of Kaufmann, taking into account the multiple reflections that occur at the particle and at the two extremities of the string. As different expressions have to be used for the motion on the two sides of the striking point, it is obvious that such a treatment would be extremely cumbrous, and indeed of impracticable length. The other method that suggests itself is that of expressing the motion that ensues on impact as the resultant of the inharmonic vibrations of the string having a load attached to it at the striking point so long as the hammer is in contact with it, and thereafter as a free periodic vibration of the usual kind. Here also a difficulty arises. For the inharmonic trigonometrical series expressing the force exerted by the particle on the string is not uniformly convergent in the neighbourhood of the discontinuities in the function expressing its sum, and it is thus not practicable directly to carry out an accurate summation of its terms to enable the duration of contact between particle and string to be found. By a judicious combination of the two methods indicated above, however, a fairly simple and straightforward process may be evolved for finding the graph of the force exerted by the hammer on the string for any position of the striking point, and thus determining the duration of contact.

In the following analysis μ is the linear density of the string, l, a, b represent respectively the length of the whole string and of the two parts into which the striking point divides it, and m is the mass of the impinging particle.

The free periods of the loaded string are determined by the values λ_1, λ_2, λ_3, etc., satisfying the equation*

$$\mu \sin \lambda_\gamma l = m\lambda_\gamma \sin \lambda_\gamma a \sin \lambda_\gamma b. \tag{1}$$

The displacement ζ at any point of the loaded string is expressed by the infinite series,

$$\zeta = \sum_{\gamma=1}^{\gamma=\infty} \phi_\gamma \sin c\lambda_\gamma t \frac{\sin \lambda_\gamma x \sin \lambda_\gamma b}{\sin \lambda_\gamma a \sin \lambda_\gamma (l-x)}, \tag{2}$$

where c is the velocity of transverse waves on the string, and the alternative expressions refer to the two parts of the string.

The constants ϕ_1, ϕ_2, etc., in (2) have to be found from the initial conditions. The system is initially without velocities or displacements except in regard to the particle of mass m, which has a velocity v. Using the notation adopted in Art. 101 of Lord Rayleigh's 'Theory of Sound,' vol. 1, we find that the displacement ζ_0 of the point struck at any instant during the impact is given by the expression

$$\zeta_0 = \sum_{\gamma=1}^{\gamma=\infty} \sin c\lambda_\gamma t \frac{mv \sin^2 \lambda_\gamma a \sin^2 \lambda_\gamma b}{c\lambda_\gamma \int \rho u_\gamma^2 \, dx}, \tag{3}$$

where

$$\int \rho u_\gamma^2 \, dx = m \sin^2 \lambda_\gamma a \sin^2 \lambda_\gamma b$$
$$+ \mu \left[\int_0^a \sin^2 \lambda_\gamma x \sin^2 \lambda_\gamma b \, dx + \int_a^l \sin^2 \lambda_\gamma a \sin^2 \lambda_\gamma (l-x) \, dx \right]. \tag{4}$$

Integrating (4) and simplifying by the aid of the relation given in (1), we obtain

$$\zeta_0 = \sum_{\gamma=1}^{\gamma=\infty} \frac{2v \sin c\lambda_\gamma t / c\lambda_\gamma}{1 + \mu/m\,(a/\sin^2 \lambda_\gamma a + b/\sin^2 \lambda_\gamma b)}. \tag{5}$$

The force $-m\dfrac{d^2\zeta_0}{dt^2}$ exerted by the particle on the string is therefore given by the equation

$$-m\frac{d^2\zeta_0}{dt^2} = \sum_{\gamma=1}^{\gamma=\infty} \frac{2mvc\lambda_\gamma \sin c\lambda_\gamma t}{1 + \mu/m\,(a/\sin^2 \lambda_\gamma a + b/\sin^2 \lambda_\gamma b)}. \tag{6}$$

Equation (6) expresses the force exerted by the particle on the string as the sum of an infinite series of simple circular functions of the time, whose frequencies are the same as that of the vibrations of the loaded string, and whose relative magnitudes depend only on the ratio of the mass of the hammer to the mass of the string, and the ratio in which the striking point divides the string. As remarked above, a difficulty arises in attempting to carry out a numerical summation of the series for all values of t, owing to the discontinuous nature of the function which the sum represents. This difficulty may, however, be evaded, and the work of numerical computation greatly simplified, by finding the magnitudes of the discontinuities in the function and the instants of time at which they occur directly from the principles of wave-propagation. This may be done in the following way.

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* Lord Rayleigh's 'Theory of Sound,' Art. 136.

At time $t=0$ the particle impinges on the wire, and two discontinuous changes of velocity, each equal to v (the initial velocity of the particle), travel out, one on each side of the string, reach the ends of the string in due course, are reflected, and return again, much in the same way as in the theory of the Helmholtzian vibrations of a bowed string. When a discontinuity reaches the particle it is reflected out again without alteration of magnitude. This follows from the fact that the particle constitutes in effect a region of infinite density on the string. Thus, at intervals of time $2\,a/c$, $4\,a/c$, etc., and again at intervals $2\,b/c$, $4\,b/c$, $6\,b/c$, etc., counting from the commencement of the impact, we have discontinuous changes of velocity reaching and being reflected from the particle. At these instants the *acceleration* of the particle suffers corresponding discontinuous changes. At the commencement of the impact the pressure exerted by the particle on the string is equal to $2\,\mu cv$, as can be shown directly from the principle of the conservation of momentum. Accordingly, at the instants $t=2\,a/c$, $4\,a/c$, etc., and also at the instants $t=2\,b/c$, $4\,b/c$, etc., the pressure exerted suffers discontinuous *increases* of $2\,\mu cv$. (If in any case the reflected waves from the two ends arrive simultaneously at the striking point, the pressure would increase by $4\,\mu cv$.) In the intervals between the arrival of the reflected waves the pressure exerted by the particle would decrease in a continuous manner defined by equation (6) above.

Now the question is, what would the series in (6) represent at the points of discontinuity, that is, when t is put equal to $2\,a/c$, $4\,a/c$, or $2\,b/c$, $4\,b/c$, etc.? It is clear that by taking a sufficient number of terms, we should obtain a sum which converges to the *mean* value of the function at these points, and for this purpose a much smaller number of terms (say 10 or 12) would suffice than would be necessary if we attempted to compute the form of the function itself in the neighbourhood of the discontinuities. Having ascertained the mean value of the function at a point of discontinuity, its two actual limiting values follow at once by adding and subtracting half the magnitude of the discontinuity, that is, μcv. (If two reflections arrive simultaneously at the striking point in any case, we have respectively to add and subtract $2\,\mu cv$.)

The graph of the continuous part of the function may be then filled in in free hand by joining up the alternate ends of successive discontinuities by smooth curves.

3. *Numerical Computation of the Force exerted by the Hammer.*

To illustrate the application of the foregoing theory to actual cases, the authors have carried out a numerical computation of the magnitudes and frequencies of the components of force exerted by the impinging particle on the string for a particular ratio of their masses ($m/\mu l = 1{\cdot}684$), and for 27 different positions of the striking point situated at intervals along the string between its end and the centre. In the light of the practical experience gained, it may be useful to indicate briefly how the work may be arranged, so as to secure sufficient accuracy with the minimum of labour.*

The first step is the determination of the values of λ_γ, which satisfy equation (1). If the mass m of the hammer be zero, these values are π/l, $2\pi/l$, $3\pi/l$, etc. On the other hand, if m be very large, λ_1 tends to zero, and the higher roots fall into two groups which tend to the limits π/a, $2\pi/a$, $3\pi/a$, etc., and π/b, $2\pi/b$, $3\pi/b$, etc., respectively. For any actual value of m, the lowest root λ_1 of equation (1) has to be found by trial. The work may be lightened when it has to be done for a large number of positions of the striking point, by first finding λ_1 by trial for three or four positions of the striking point at wide intervals on the string, and then finding it for the other points by graphical interpolation and testing the values thus obtained by actual substitution in the equation (1). The calculation of the higher roots of this equation is a simpler task. For, to a first approximation, λ_γ is equal to either $p\pi/a$ or $q\pi/b$, where p and q are integers. To a second approximation, λ_γ is equal to $p\pi/a$ or $q\pi/b$, plus a correction which is either $\mu/m\pi p$ or $\mu/m\pi q$. (In special cases, where $p\pi/a = q\pi/b$, the correction to the value of λ_γ is $\mu(p+q)/m\pi pq$.) The values of λ_4, λ_5, λ_6, etc., thus obtained are generally sufficiently accurate, but the values of λ_2, λ_3 may require further improvement by actual test against equation (1), especially when the striking point is close to the end of the string.

The second step is the determination of the magnitudes of the components of force from equation (6). The fact that $\sin\lambda_\gamma a$ and $\sin\lambda_\gamma b$ appear both in equation (1) and in (6), helps to save some labour. Except when $\gamma = 1$, one of these quantities, that is either $\sin\lambda_\gamma a$ or $\sin\lambda_\gamma b$, is generally small in comparison with the other, and the magnitude of the component of force in (6) is practically determined by the smaller of the two quantities, which alone

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* The authors wish here to acknowledge the assistance they have received from Mr. Durgadas Banerji, M.Sc., in carrying out part of the numerical work.

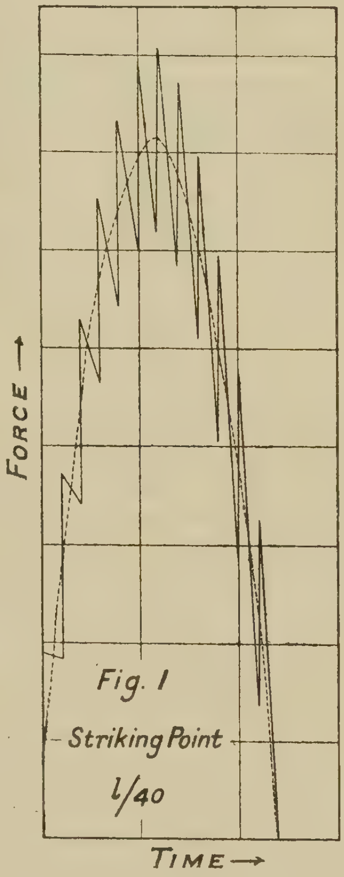
requires to be determined with accuracy. This may be found from (1), so as *exactly* to satisfy this equation, the approximate value of λ_γ (ascertained as indicated in the preceding paragraph) being used for the computation of the other quantities in the equation. The results thus obtained may be substituted in the denominator of (6), and enable the force-components to be accurately determined.

It is of interest to notice the manner in which the computed magnitudes and frequencies of the components of force are found to depend on the position of the striking point. Since the frequencies of the components are those of a string carrying a load at the point of impact, they form a series of which the terms (in accordance with a well-known principle) are separated by the natural frequencies of the unloaded string. The frequency of the rth component of force is thus intermediate between that of the rth and $(r-1)$th harmonics of the string, and is a maximum when the striking point is at a node of the rth harmonic and a minimum when at a node of the $(r-1)$th harmonic.

The magnitudes of the components of force similarly fluctuate, but to a much larger extent than their frequencies, and in the opposite direction. Thus the rth component of force is zero when the striking point is at a node of the rth harmonic, and is a maximum when it is a node of the $(r-1)$th harmonic, being largest when the node is that nearest the end of the string. For example, the ninth component of force which is zero when the striking point is at $l/9$, rises rapidly to a large maximum when it is shifted to $l/8$, and falls quickly again to a small fraction of this value when it is further shifted to $l/7$ or $l/6$ or $l/5$. It shows similar fluctuations when the striking point is moved still nearer the centre of the string, becoming zero when the striking point is at $2l/9$ or $3l/9$, and reaching large values when it is at $2l/8$, $3l/8$, or $4l/8$, but these maxima are not so great as the first. The manner in which the frequencies and magnitudes of the components of force change when the striking point approaches very near one end of the string is specially worthy of notice. Here the first component (which elsewhere is generally much larger than the rest) falls off rapidly in magnitude, and as the striking point is brought nearer and nearer the end, the second, third, and higher components increase, and become in succession the largest in magnitude, and each in turn then falls off, giving precedence, as it were, to the next component in the series. The maximum value of each component is reached when its frequency falls to the minimum value and begins again to rise steeply.

4. *Graphical Determination of the Duration of Contact.*

Using the computed values of the magnitudes and frequencies of the components of force, the graph representing the discontinuous fluctuations with time of the force exerted by the impinging particle on the string may be plotted in the manner explained in a previous section. The point at which the graph cuts the axis of time gives at once the duration of contact. Figs. 1 and 2 represent the force-time graphs for the two cases in which the striking point is at $l/40$ and at $l/9$ respectively. These diagrams are given to illustrate the manner in which the form of the graphs and the duration of contact alter as the striking point is removed further and further from the end. In both of these cases, the hammer loses contact with the string long before the wave started by the impact has had time to reach the farther end of the string and to return after reflection to the striking point. The discontinuities appearing in the graphs accordingly represent the successive reflections of the waves between the striking point and the *nearer* end of the string. It will be noticed that in fig. 1 12 discontinuities appear which are close together, and in fig. 2 there are only six which are further apart. The effect of removing the striking point further from the end of the string is to *increase* the duration of contact in a continuous manner, so long as the number of discontinuities in the graph remains unaltered. At the successive stages, however, at which the number of discontinuities in the graph decreases by unity, the duration of contact *decreases* by a finite amount in a discontinuous manner, these jumps being the greater and further apart, the more distant the striking point is from the end.



It is thus clear that the duration of contact is a discontinuous function of the position of the striking point.

When the striking point is so far removed from the end of the string that reflections from both ends of the string have to be taken into account, then either a decrease or an increase in the duration of contact may take place in a discontinuous manner: the former when the number of discontinuities in the graph goes up by unity with the change in the position of the striking point, and the latter when it goes down by the same amount. The whole course of values for the duration of contact for 27 different positions of the striking point between the end and centre of the string is shown in fig. 3.

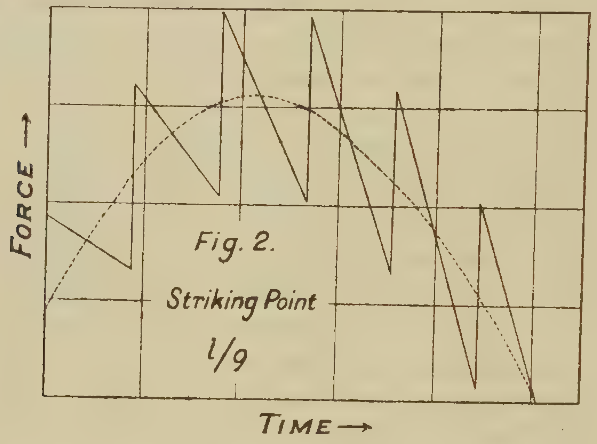


Fig. 2.

Striking Point

l/9

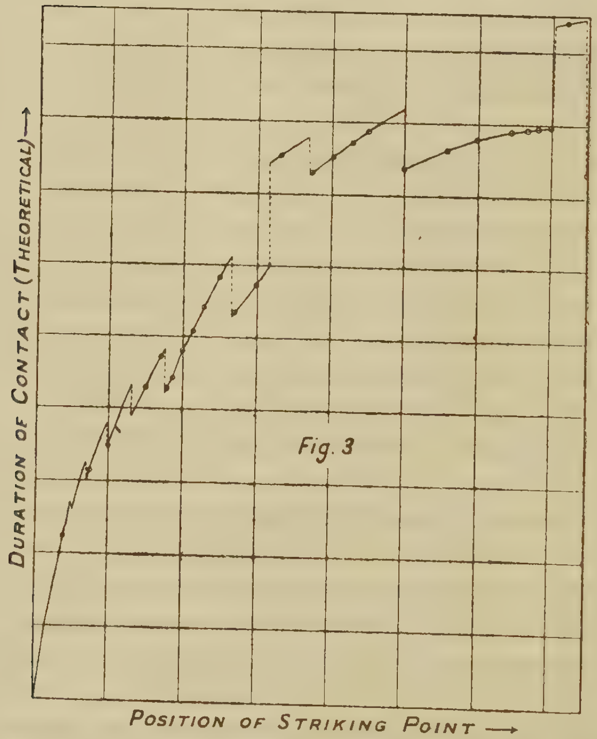


Fig. 3

The duration of contact found by this method agrees exactly with that found from Kaufmann's treatment for the case in which the striking point is at the centre of the string. There is also sensible agreement of the duration of contact with that found by the approximate method of Kaufmann when the striking point is sufficiently close to the end of the string; say at $l/40$ or $l/20$. Elsewhere, Kaufmann's approximate treatment fails.

Figs. 1 and 2 also illustrate another feature which is worthy of notice. The dotted lines in the two diagrams represent the graphs of the force exerted by the impinging particle on the string, if the more rapid periodic fluctuations which may be regarded as due to the vibrations of the shorter segment of the string are neglected. It is seen that the two dotted curves are distinctly unsymmetrical in shape and follow in fact the outline of a damped harmonic curve. This is in agreement with the approximate theory given by Kaufmann.

5. *Some Experimental Results.*

The result indicated by the foregoing theory that the duration of contact is a discontinuous function of the position of the striking point appeared worthy of an experimental test. This was attempted in the following way. A steel wire 150 cm. long, was nickeled and silver-plated so as to ensure its surface giving good electric contact, and stretched over the bridges of a sonometer. The linear density of the wire was 0·095 grm. per centimetre. A small solid brass cylinder was mounted at the end of a light pivoted shaft, and could be caused to impinge transversely on the wire. Immediately on impact, the cylinder and shaft of the hammer completed an electric circuit through the wire and a sensitive Leeds and Northrup ballistic galvanometer. Three or four readings of the throw of the galvanometer were taken for each of a large number of positions of the striking point, and the average struck. To secure that the variable electric resistance at the point of contact should not influence the results, a non-inductive resistance of half a megohm was included in the circuit. The results for two different masses of the impinging cylinder have been plotted in fig. 4.

It is obvious from the experimental curves that the duration of contact does not continuously increase as the striking point is removed further and further from the end of the string, but that it is subject to rapid fluctuations, the magnitude of which increases as the striking point is moved away from the end. Of the two curves shown in fig. 4, the upper relates to the case of an impinging cylinder having a mass of 24 grm., and the second of a cylinder having a mass of 16 grm., the figures in each case including a correction for the inertia of the shaft calculated after the manner of Kaufmann. The ratio of the mass of the hammer to the mass of the string for the upper of the two curves in fig. 4 is the same as that for which the theoretical computations have been carried out and plotted in fig. 3, and the general resemblance between the computed and observed curves is obvious. Why there is not a much closer agreement is an open question.

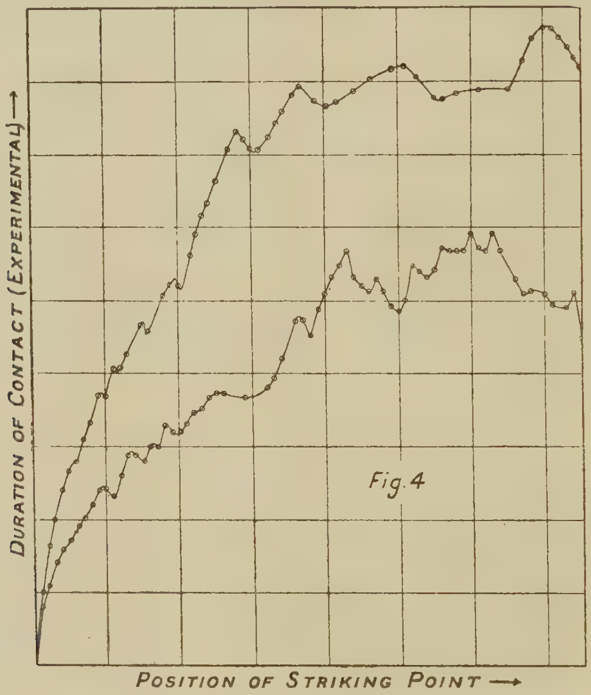


Fig. 4

It must be remembered that, in many respects, the experimental arrangements do not strictly reproduce the conditions assumed in the theoretical calculations. The finite size of the cylinder and elastic flexure of the shaft, the stiffness of the wire and its yielding at the ends, and the effect of gravity on the motion of the impinging cylinder, are factors which probably influence the results in an appreciable degree. There is no doubt, however, that the experimental results shown in fig. 4, broadly speaking, confirm the correctness of the theoretical results, and the suitability of the method of calculation set out in the paper.

From an acoustical point of view, a further development that would be of interest is the theoretical determination (and comparison with experiment) of the manner in which the amplitudes of the fundamental and higher harmonic components of the vibration of the string excited by impact depend on the mass of the hammer and the position of its striking point over the entire possible range.* It may be remarked that equations (2) and (5) of the paper determine the motion at every point of the string *during the continuance of the impact*. The motion, after the hammer has left the string, would have to be separately determined. This could no doubt be found from the known displacements and velocities at various points of the string at the instant the hammer leaves it. One way of doing this is by a geometrical method similar to that used by Kaufmann. A better method, however, would be to express the motion resulting from impact in terms of the forces exerted by the impinging particle and the duration of contact.† The graphs from which the duration of contact is determined would be very useful in this connection, as the necessary integrations could be carried out mechanically with the aid of these curves.

6. *Summary and Conclusion.*

The present paper is chiefly concerned with a revision and extension of the theory of the impact of the pianoforte hammer developed by Kaufmann. It is pointed out that the approximate method used by Kaufmann, in which he assumes that the part of the string between the striking point and the nearer end remains straight so long as the hammer is in contact is unsatisfactory, and cannot be regarded as applicable when this part of the string forms an appreciable fraction of the whole. It is shown how this assumption may be dispensed with, and the general case, in which an inelastic particle impinges at any point on the string, may be dealt with rigorously and subjected to numerical computation. The manner in which the force exerted by the impinging particle varies is determined, partly from the functional solutions of the equations of wave-propagation, and partly from the theory of normal vibrations. Numerical computations have been carried out of the components of force for a particular ratio of the masses of the string, and of the impinging particle, and for 27 different positions of the striking point, and the duration of contact is deduced by a graphical method. An interesting result obtained is that the duration of contact does not continually increase as the striking point is removed away from the end of the string, but is subject to discontinuous fluctuations. Experimental work, broadly speaking, confirms this indication of theory.

The present paper is preliminary to a more complete investigation, in which the authors hope to develop fully various points in the theory of the pianoforte, especially (1) the manner in which the amplitudes of the component partial vibrations of the string depend on the position of the striking point; (2) the effect of the mass and elasticity of the hammer; (3) the characteristics of the coupled vibrations of the string and soundboard of the pianoforte; (4) the manner in which these vibrations decay by communication of energy to the atmosphere; and (5) the theoretical determination of the quality of pianoforte tone. Further work on these points, and experimental tests on an actual pianoforte, are now in progress.

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* The choice of the position of the striking point actually adopted in the pianoforte is no doubt determined by its influence on the useful effect produced by the impact of the hammer. See G. H. Berry, 'Phil. Mag.,' April, 1910.

† Arts. 128 and 130, Rayleigh's 'Theory of Sound' vol. 1.

In conclusion, the authors wish to thank Dr. Gilbert Walker, F.R.S., who has taken a lively interest in their work, for his kindness in bringing it before the Royal Society.

Plane Strain: the Direct Determination of Stress.

By S. D. Carothers, Assoc.M.Inst.C.E.

(Communicated by Prof. A. E. H. Love, F.R.S. Received December 9, 1919.)

(1) The advantages of the direct determination of the stresses in an elastic solid have been pointed out by Prof. J. H. Michell*. The principal line of attack in the case of plane strain has been by aid of the well-known stress function method, by which the stresses are determined from a single stress function χ, of x and y only, satisfying

$$\nabla_1{}^4\chi = 0,$$

where
$$\nabla_1{}^2 = \frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}. \qquad (1)$$

The lines along which further advance might have been expected, and the difficulties which have been met with, are discussed by Prof. A. E. H. Love.†

It seems to the writer, however, that a point of very considerable importance has been overlooked, viz., that the stress function method gives a set of stresses which can in most cases be resolved into two distinct sets, each of which leads to strains satisfying the identical relations between the strain components.

For example, if ϕ is a plane harmonic function, $\chi = (x^2+y^2)\phi$ satisfies $\nabla_1{}^4\chi = 0$, and the stresses derived from this by the well-known formulæ

$$\widehat{xx} = \frac{\partial^2\chi}{\partial y^2}, \quad \widehat{yy} = \frac{\partial^2\chi}{\partial x^2}, \quad \text{and} \quad \widehat{xy} = -\frac{\partial^2\chi}{\partial x\partial y}, \qquad (2)$$

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* 'Proc. Lond. Math. Soc.,' vol. 31, p. 100.

† 'Math. Theory of Elasticity,' 2nd Edition, p. 211.

can be expressed as follows:—

$$\left.\begin{aligned}\widehat{xx} &= 2(\phi+\phi')+\left(y\frac{\partial}{\partial y}-x\frac{\partial}{\partial x}\right)(\phi+\phi') \\ \widehat{yy} &= 2(\phi+\phi')-\left(y\frac{\partial}{\partial y}-x\frac{\partial}{\partial x}\right)(\phi+\phi') \\ \widehat{xy} &= \qquad\qquad\quad -\left(y\frac{\partial}{\partial x}+x\frac{\partial}{\partial y}\right)(\phi+\phi')\end{aligned}\right\}, \tag{3}$$

where $\phi' = x\partial\phi/\partial x+y\partial\phi/\partial y.$

Now, on examination it will be found, ϕ and ϕ' being each harmonic, that $\phi+\phi_1$ can be replaced by any plane harmonic function and the identical relation between the strain components will be preserved. This has led the writer to an examination of the various independent types of possible solutions which can be derived by operating direct on plane harmonic functions, instead of operating on χ, which in general leads to functions of a complicated character. For the purpose of building up a solution in plane strain by synthesis the advantages of this method will be obvious.

(2) The stress equations of equilibrium in rectangular, in plane polar, and in orthogonal curvilinear co-ordinates, together with the identical relations between the strain components in each case, will be set out in order. Using the notation of Love, 'Elasticity,' 2nd edition, and omitting volume force, these are as follows:—

The stress equations in rectangular co-ordinates are

$$\left.\begin{aligned}\frac{\partial}{\partial x}\widehat{xx}+\frac{\partial}{\partial y}\widehat{xy} &= 0 \\ \frac{\partial}{\partial x}\widehat{xy}+\frac{\partial}{\partial y}\widehat{yy} &= 0\end{aligned}\right\}. \tag{4}$$

The identical relation between the strain components is

$$\frac{\partial^2}{\partial y^2}\epsilon_{xx}+\frac{\partial^2}{\partial x^2}\epsilon_{yy} = \frac{\partial^2}{\partial x\partial y}\epsilon_{xy}. \tag{5}$$

In plane polars the similar equations are

$$\left.\begin{aligned}\frac{\partial}{\partial r}\widehat{rr}+\frac{1}{r}\frac{\partial}{\partial\theta}\widehat{r\theta}+\frac{\widehat{rr}-\widehat{\theta\theta}}{r} &= 0 \\ \frac{\partial}{\partial r}\widehat{r\theta}+\frac{1}{r}\frac{\partial}{\partial\theta}\widehat{\theta\theta}+\frac{2\widehat{r\theta}}{r} &= 0\end{aligned}\right\}, \tag{6}$$

and

$$\left(\frac{1}{r^2}\frac{\partial^2}{\partial\theta^2}-\frac{1}{r}\frac{\partial}{\partial r}\right)\epsilon_{rr}+\left(\frac{\partial^2}{\partial r^2}+\frac{2}{r}\frac{\partial}{\partial r}\right)\epsilon_{\theta\theta}-\frac{1}{r^2}\frac{\partial^2}{\partial r\partial\theta}(r\epsilon_{r\theta}) = 0. \tag{7}$$

In orthogonal curvilinears the equations are

$$h_1\frac{\partial}{\partial\alpha}\widehat{\alpha\alpha}+h_2\frac{\partial}{\partial\beta}\widehat{\alpha\beta}+2h_1h_2\widehat{\alpha\beta}\,\frac{\partial}{\partial\beta}\left(\frac{1}{h_1}\right)+h_1h_2(\widehat{\alpha\alpha}-\widehat{\beta\beta})\,\frac{\partial}{\partial\alpha}\left(\frac{1}{h_2}\right)=0,$$

$$h_1\frac{\partial}{\partial\alpha}\widehat{\alpha\beta}+h_2\frac{\partial}{\partial\beta}\widehat{\beta\beta}+2h_1h_2\widehat{\alpha\beta}\,\frac{\partial}{\partial\alpha}\left(\frac{1}{h_2}\right)-h_1h_2(\widehat{\alpha\alpha}-\widehat{\beta\beta})\,\frac{\partial}{\partial\beta}\left(\frac{1}{h_1}\right)=0,$$

but these can be transformed to

$$\left.\begin{aligned}h_2\frac{\partial}{\partial\alpha}\left(\frac{\widehat{\alpha\alpha}}{h_2^2}\right)+h_1\frac{\partial}{\partial\beta}\left(\frac{\widehat{\alpha\beta}}{h_1^2}\right)-(\widehat{\alpha\alpha}+\widehat{\beta\beta})\,\frac{\partial}{\partial\alpha}\left(\frac{1}{h_2}\right)=0\\ h_2\frac{\partial}{\partial\alpha}\left(\frac{\widehat{\alpha\beta}}{h_2^2}\right)+h_1\frac{\partial}{\partial\beta}\left(\frac{\widehat{\beta\beta}}{h_1^2}\right)-(\widehat{\alpha\alpha}+\widehat{\beta\beta})\,\frac{\partial}{\partial\beta}\left(\frac{1}{h_1}\right)=0\end{aligned}\right\}. \qquad (8)$$

The identical relation between the strain components is

$$\frac{\partial}{\partial\alpha}\left[h_1h_2\frac{\partial}{\partial\alpha}\left(\frac{\epsilon_{\alpha\alpha}-\epsilon_{\beta\beta}}{h_2^2}\right)+h_1^2\,\frac{\partial}{\partial\beta}\left(\frac{\epsilon_{\alpha\beta}}{h_1^2}\right)\right]$$
$$+\frac{\partial}{\partial\beta}\left[h_1h_2\frac{\partial}{\partial\beta}\left(\frac{\epsilon_{\beta\beta}-\epsilon_{\alpha\alpha}}{h_1^2}\right)+h_2^2\,\frac{\partial}{\partial\alpha}\left(\frac{\epsilon_{\alpha\beta}}{h_2^2}\right)\right]=0. \qquad (9)$$

Stress Equations.

(3) As regards equations (4) and (5) there are four solutions which, for convenience of space, may be written in the form:—

$$\left.\begin{aligned}\widehat{xx}&=a\phi+b\psi+c\left(\phi-x\frac{\partial\phi}{\partial x}\right)+d\left(\phi+y\frac{\partial\phi}{\partial y}\right)\\ \widehat{yy}&=-a\phi-b\psi+c\left(\phi+x\frac{\partial\phi}{\partial x}\right)+d\left(\phi-y\frac{\partial\phi}{\partial y}\right)\\ \widehat{xy}&=-a\psi+b\phi+c\left(\quad-x\frac{\partial\phi}{\partial y}\right)+d\left(\quad-y\frac{\partial\phi}{\partial x}\right)\end{aligned}\right\}; \qquad (10)$$

where a, b, c, and d are any constants. Equations (10) will be referred to as the "a," "b," etc., solutions. In the "a" and "b" solutions $\phi+i\psi=f(x+iy)$, and in the "c" and "d" solutions ϕ is any plane harmonic function. If $c=d$ the difference between the "c" and "d" solutions is of the same type as the "a" solution.

(4) As regards equations (6) and (7) the solutions are

$$\left.\begin{aligned}\widehat{rr}&=a_1\phi/r^2+b_1\psi/r^2+c_1\left(2\phi-r\frac{\partial\phi}{\partial r}\right)\\ \widehat{\theta\theta}&=-a_1\phi/r^2-b_1\psi/r^2+c_1\left(2\phi+r\frac{\partial\phi}{\partial r}\right)\\ \widehat{r\theta}&=-a_1\psi/r^2+b_1\phi/r^2+c_1\left(\quad-\frac{\partial\phi}{\partial\theta}\right)\end{aligned}\right\}; \qquad (11)$$

where the same meaning is attached to ϕ and ψ as obtains in equations (10).

(5) To obtain the solution of equations (8) and (9), when $\widehat{\alpha\alpha}+\widehat{\beta\beta}=0$, a direct solution must be found. If ϕ and ψ are conjugate functions, such that $\phi+i\psi=f(x+iy)$, it is easily shown that

$$\left.\begin{aligned} h_1\frac{\partial\phi}{\partial\alpha}-h_2\frac{\partial\psi}{\partial\beta}&=0\\ \text{and}\qquad h_1\frac{\partial\psi}{\partial\alpha}+h_2\frac{\partial\phi}{\partial\beta}&=0\end{aligned}\right\},\tag{12}$$

from which it follows that

$$h_1^2\left[\left(\frac{\partial\phi}{\partial\alpha}\right)^2-\left(\frac{\partial\psi}{\partial\alpha}\right)^2\right]=-h_2^2\left[\left(\frac{\partial\phi}{\partial\beta}\right)^2-\left(\frac{\partial\psi}{\partial\beta}\right)^2\right],$$

and

$$h_1^2\frac{\partial\phi}{\partial\alpha}\frac{\partial\psi}{\partial\alpha}=-h_2^2\frac{\partial\phi}{\partial\beta}\cdot\frac{\partial\psi}{\partial\beta}.$$

When $\widehat{\alpha\alpha}+\widehat{\beta\beta}=0$, equations (8) and (9) are identically satisfied by the solutions

$$\left.\begin{aligned} \widehat{\alpha\alpha}&=-a_2h_2^2\left[\left(\frac{\partial\phi}{\partial\beta}\right)^2-\left(\frac{\partial\psi}{\partial\beta}\right)^2\right]\\ \widehat{\beta\beta}&=-a_2h_1^2\left[\left(\frac{\partial\phi}{\partial\alpha}\right)^2-\left(\frac{\partial\psi}{\partial\alpha}\right)^2\right]\\ \widehat{\alpha\beta}&=-2a_2h_1^2\frac{\partial\phi}{\partial\alpha}\frac{\partial\psi}{\partial\alpha}\end{aligned}\right\},\tag{13}$$

and

$$\left.\begin{aligned} \widehat{\alpha\alpha}&=-2b_2h_2^2\frac{\partial\phi}{\partial\beta}\frac{\partial\psi}{\partial\beta}\\ \widehat{\beta\beta}&=-2b_2h_1^2\frac{\partial\phi}{\partial\alpha}\frac{\partial\psi}{\partial\alpha}\\ \widehat{\alpha\beta}&=\quad b_2h_1^2\left[\left(\frac{\partial\phi}{\partial\alpha}\right)^2-\left(\frac{\partial\psi}{\partial\alpha}\right)^2\right]\end{aligned}\right\}.\tag{14}$$

These are equivalent respectively to the same stress systems as the rectangular sets

$$\left.\begin{aligned} \widehat{xx}&=\quad a_2\left[\left(\frac{\partial\phi}{\partial x}\right)^2-\left(\frac{\partial\psi}{\partial x}\right)^2\right]\\ \widehat{yy}&=-a_2\left[\left(\frac{\partial\phi}{\partial x}\right)^2-\left(\frac{\partial\psi}{\partial x}\right)^2\right]\\ \widehat{xy}&=-2a_2\frac{\partial\phi}{\partial x}\frac{\partial\psi}{\partial x}\end{aligned}\right\};\tag{15}$$

and

$$\left.\begin{aligned} \widehat{xx} &= 2b_2\frac{\partial\phi}{\partial x}\frac{\partial\psi}{\partial x} \\ \widehat{yy} &= -2b_2\frac{\partial\phi}{\partial x}\frac{\partial\psi}{\partial x} \\ \widehat{xy} &= -b_2\left[\left(\frac{\partial\phi}{\partial x}\right)^2-\left(\frac{\partial\psi}{\partial x}\right)^2\right] \end{aligned}\right\} . \qquad (16)$$

The above stress systems are the two-dimensional analogue of Maxwell's well-known three-dimensional stress system, but the objections to the latter* as applying to an elastic body slightly strained from a state of no stress and free from body forces, as contemplated in equations (8) of this paper, do not apply to two-dimension stress. Other solutions when $\Delta = 0$ will be referred to later.

(6) To obtain a direct solution of equations (8) and (9) when $\widehat{\alpha\alpha}+\widehat{\beta\beta}$ is not zero appears to the writer to be a matter of great difficulty, but this can be overcome by the transformation of the "*c*" and "*d*" solutions of equations (10) to curvilinear co-ordinates. It can also be overcome by the direct differentiation of $\chi = (x^2+y^2)\,\phi$. Using first the transformation method, the "*c*" solution gives stresses on any orthogonal curves α, β.

$$\left.\begin{aligned} \widehat{\alpha\alpha} &= \phi - x\frac{\partial\alpha}{\partial x}\frac{\partial\phi}{\partial\alpha} + x\frac{\partial\beta}{\partial x}\frac{\partial\phi}{\partial\beta} \\ \widehat{\beta\beta} &= \phi + x\frac{\partial\alpha}{\partial x}\frac{\partial\phi}{\partial\alpha} - x\frac{\partial\beta}{\partial x}\frac{\partial\phi}{\partial\beta} \\ \widehat{\alpha\beta} &= \phantom{\phi+{}} x\frac{\partial\alpha}{\partial y}\frac{\partial\phi}{\partial\alpha} - x\frac{\partial\beta}{\partial y}\frac{\partial\phi}{\partial\beta} \end{aligned}\right\} . \qquad (17)$$

The "*d*" solution gives stresses on α, β as follows:—

$$\left.\begin{aligned} \widehat{\alpha\alpha} &= \phi - y\frac{\partial\alpha}{\partial y}\frac{\partial\phi}{\partial\alpha} + y\frac{\partial\beta}{\partial y}\frac{\partial\phi}{\partial\beta} \\ \widehat{\beta\beta} &= \phi + y\frac{\partial\alpha}{\partial y}\frac{\partial\phi}{\partial\alpha} - y\frac{\partial\beta}{\partial y}\frac{\partial\phi}{\partial\beta} \\ \widehat{\alpha\beta} &= -y\frac{\partial\alpha}{\partial x}\frac{\partial\phi}{\partial\alpha} + y\frac{\partial\beta}{\partial x}\frac{\partial\phi}{\partial\beta} \end{aligned}\right\} . \qquad (18)$$

If the above solutions are added the stresses are

$$\left.\begin{aligned} \widehat{\alpha\alpha} &= 2\phi - \tfrac{1}{2}h_1^2\frac{\partial f}{\partial\alpha}\frac{\partial\phi}{\partial\alpha} + \tfrac{1}{2}h_2^2\frac{\partial f}{\partial\beta}\frac{\partial\phi}{\partial\beta} \\ \widehat{\beta\beta} &= 2\phi + \tfrac{1}{2}h_1^2\frac{\partial f}{\partial\alpha}\frac{\partial\phi}{\partial\alpha} - \tfrac{1}{2}h_2^2\frac{\partial f}{\partial\beta}\frac{\partial\phi}{\partial\beta} \\ \widehat{\alpha\beta} &= -\tfrac{1}{2}h_1h_2\left(\frac{\partial f}{\partial\alpha}\frac{\partial\phi}{\partial\beta}+\frac{\partial f}{\partial\beta}\frac{\partial\phi}{\partial\alpha}\right) \end{aligned}\right\} ; \qquad (19)$$

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* See Love, 'Elasticity,' 2nd Edition, pp. 82 and 133.

where $f = x^2+y^2$ since

$$x\frac{\partial\alpha}{\partial x}+y\frac{\partial\alpha}{\partial y} = h_1^2\left(x\frac{\partial x}{\partial\alpha}+y\frac{\partial y}{\partial\alpha}\right) = \tfrac{1}{2}h_1^2\frac{\partial f}{\partial\alpha}.$$

(7) If α and β are homogeneous and of the nth degree in x and y equations (19) take the form

$$\left.\begin{aligned}\widehat{\alpha\alpha} &= 2\phi-n\alpha\frac{\partial\phi}{\partial\alpha}+n\beta\frac{\partial\phi}{\partial\beta}\\ \widehat{\beta\beta} &= 2\phi+n\alpha\frac{\partial\phi}{\partial\alpha}-n\beta\frac{\partial\phi}{\partial\beta}\\ \widehat{\alpha\beta} &= \quad -n\frac{h_2}{h_1}\alpha\frac{\partial\phi}{\partial\beta}-n\frac{h_1}{h_2}\beta\frac{\partial\phi}{\partial\alpha}\end{aligned}\right\} \qquad (20)$$

(8) Conjugate functions. When the curves α and β are conjugate functions, the "a" and "b" solutions take the form

$$\left.\begin{aligned}\widehat{\alpha\alpha} &= \quad a_3h^2\phi+b_3h^2\psi\\ \widehat{\beta\beta} &= -a_3h^2\phi-b_3h^2\psi\\ \widehat{\alpha\beta} &= -a_3h^2\psi+b_3h^2\phi\end{aligned}\right\}; \qquad (21)$$

when $\widehat{\alpha\alpha}+\widehat{\beta\beta} = 0$ or $\Delta = 0$.

When Δ is not equal to zero, solutions may be easily obtained from the general results of equations (19) by writing $h_1 = h_2 = h$, and this solution need not be repeated.

(9) To obtain the stresses in orthogonal curvilinears by direct differentiation, take the axes of x and y normal to the curves α and β at any point in the $\alpha\beta$ region. If χ is a solution of

$$\nabla_1^4\chi = 0,$$

the stresses will be given by

$$\widehat{xx}=\widehat{\alpha\alpha} = \frac{\partial^2\chi}{\partial y^2}, \text{ etc.},$$

and it remains to find $\partial^2\chi/\partial x^2$, etc., in terms of curvilinears.

There is no difficulty in showing that if V is any function of α, β, and also of x, y

$$\left.\begin{aligned}\frac{\partial^2 V}{\partial y^2} &= h_2^2\frac{\partial^2 V}{\partial\beta^2}+h_2\frac{\partial h_2}{\partial\beta}\frac{\partial V}{\partial\beta}-\frac{h_1^2}{h_2}\frac{\partial h_2}{\partial\alpha}\frac{\partial V}{\partial\alpha}\\ \frac{\partial^2 V}{\partial x^2} &= h_1^2\frac{\partial^2 V}{\partial\alpha^2}+h_1\frac{\partial h_1}{\partial\alpha}\frac{\partial V}{\partial\alpha}-\frac{h_2^2}{h_1}\frac{\partial h_1}{\partial\beta}\frac{\partial V}{\partial\beta}\\ -\frac{\partial^2 V}{\partial x\partial y} &= -h_1h_2\left[\frac{\partial^2 V}{\partial\alpha\partial\beta}+\frac{1}{h_1}\frac{\partial h_1}{\partial\beta}\frac{\partial V}{\partial\alpha}+\frac{1}{h_2}\frac{\partial h_2}{\partial\alpha}\frac{\partial V}{\partial\beta}\right]\end{aligned}\right\}. \qquad (22)$$

If V satisfies $\nabla_1^4 V = 0$, $\widehat{\alpha\alpha}$, $\widehat{\beta\beta}$, and $\widehat{\alpha\beta}$ will be given by equations (22) respectively, and if V is harmonic equations (22) will be a solution of equations (8) and (9) when $\Delta = 0$.

(10) If $\chi = (x^2+y^2)\phi = f \,.\, \phi$, where $f = x^2+y^2$, axes may be selected at the origin parallel to the normals to the curves α and β at any point. We have

$$\left.\begin{aligned}\frac{\partial^2\chi}{\partial x^2} = &\left(h_1{}^2\frac{\partial^2 f}{\partial\alpha^2}+h_1\frac{\partial h_1}{\partial\alpha}\frac{\partial f}{\partial\alpha}-\frac{h_2{}^2}{h_1}\frac{\partial h_1}{\partial\beta}\frac{\partial f}{\partial\beta}\right)\,.\,\phi \\ &+\left(h_1{}^2\frac{\partial^2\phi}{\partial\alpha_2}+h_1\frac{\partial h_1}{\partial\alpha}\frac{\partial\phi}{\partial\alpha}-\frac{h_2{}^2}{h_1}\frac{\partial h_1}{\partial\beta}\frac{\partial\phi}{\partial\beta}\right)\,.\,f \\ &+2h_1{}^2\frac{\partial f}{\partial\alpha}\frac{\partial\phi}{\partial\alpha}\end{aligned}\right\}. \qquad (23)$$

It is seen at once that

$$h_1{}^2\frac{\partial^2 f}{\partial\alpha^2}+h_1\frac{\partial h_1}{\partial\alpha}\frac{\partial f}{\partial\alpha}-\frac{h_2{}^2}{h_1}\frac{\partial h_1}{\partial\beta}\frac{\partial f}{\partial\beta} = 2,$$

and it is easily shown that

$$4f = h_1{}^2\left(\frac{\partial f}{\partial\alpha}\right)^2+h_2{}^2\left(\frac{\partial f}{\partial\beta}\right)^2,$$

and from these and similar relations it can be shown that, if ϕ is an harmonic function, the above value of $\partial^2\chi/\partial x^2$ can be expressed in the form

$$\begin{aligned}\frac{\partial^2\chi}{\partial x^2} = 2\phi&+h_1{}^2\frac{\partial f}{\partial\alpha}\frac{\partial\phi}{\partial\alpha}+h_2{}^2\frac{\partial f}{\partial\beta}\frac{\partial\phi}{\partial\beta} \\ &+\tfrac{1}{4}\left(h_1{}^2\frac{\partial f}{\partial\alpha}\frac{\partial}{\partial\alpha}-h_2{}^2\frac{\partial f}{\partial\beta}\frac{\partial}{\partial\beta}\right)\left(2\phi+h_1{}^2\frac{\partial f}{\partial\alpha}\frac{\partial\phi}{\partial\alpha}+h_2{}^2\frac{\partial f}{\partial\beta}\frac{\partial\phi}{\partial\beta}\right),\end{aligned} \qquad (24)$$

and similarly $\partial^2\chi/\partial y^2$ and $-\partial^2\chi/\partial x\partial y$ can be found.

If we write
$$2\phi_1 = 2\phi+h_1{}^2\frac{\partial f}{\partial\alpha}\frac{\partial\phi}{\partial\alpha}+h_2{}^2\frac{\partial f}{\partial\beta}\frac{\partial\phi}{\partial\beta}, \qquad (25)$$

the results are as follows :—

$$\left.\begin{aligned}\widehat{\alpha\alpha} &= 2\phi_1-\tfrac{1}{2}\left(h_1{}^2\frac{\partial f}{\partial\alpha}\frac{\partial}{\partial\alpha}-h_2{}^2\frac{\partial f}{\partial\beta}\frac{\partial}{\partial\beta}\right)\phi_1 \\ \widehat{\beta\beta} &= 2\phi_1+\tfrac{1}{2}\left(h_1{}^2\frac{\partial f}{\partial\alpha}\frac{\partial}{\partial\alpha}-h_2{}^2\frac{\partial f}{\partial\beta}\frac{\partial}{\partial\beta}\right)\phi_1 \\ \widehat{\alpha\beta} &= \qquad -\tfrac{1}{2}h_1h_2\left(\frac{\partial f}{\partial\alpha}\frac{\partial}{\partial\beta}+\frac{\partial f}{\partial\beta}\frac{\partial}{\partial\alpha}\right)\phi_1\end{aligned}\right\}. \qquad (26)$$

It is clear from the form and origin of these results that ϕ_1 is harmonic if ϕ is harmonic, and thus it is seen at once from equation (25) that

$$h_1{}^2\frac{\partial f}{\partial\alpha}\frac{\partial\phi}{\partial\alpha}+h_2{}^2\frac{\partial f}{\partial\beta}\frac{\partial\phi}{\partial\beta}$$

is also harmonic if ϕ is harmonic.

It follows from this that ϕ_1 can be replaced by any plane harmonic function, and the results obtained here are precisely the same as those given in equations (19).

(11) Adopting the notation of $\widehat{\alpha\alpha}_\phi$, $\widehat{\beta\beta}_\phi$, and $\widehat{\alpha\beta}_\phi$, for the stresses when V is replaced by ϕ in equations (22), and now in the same equations, replacing V by $\phi^2-\psi^2$, where $\phi+i\psi=f(x+iy)$, we obtain

$$\widehat{\alpha\alpha} = 2\left[h_2^2\left\{\left(\frac{\partial\phi}{\partial\beta}\right)^2-\left(\frac{\partial\psi}{\partial\beta}\right)^2\right\}+\phi\,.\,\widehat{\alpha\alpha}_\phi-\psi\widehat{\alpha\alpha}_\psi\right],$$

with similar results for $\widehat{\beta\beta}$ and $\widehat{\alpha\beta}$. Taking account of the solution of equations (13) we deduce at once that

$$\begin{aligned}\widehat{\alpha\alpha} &= \phi\widehat{\alpha\alpha}_\phi-\psi\widehat{\alpha\alpha}_\psi,\\ \widehat{\beta\beta} &= \phi\widehat{\beta\beta}_\phi-\psi\widehat{\beta\beta}_\psi,\\ \widehat{\alpha\beta} &= \phi\widehat{\alpha\beta}_\phi-\psi\widehat{\alpha\beta}_\psi,\end{aligned}$$

is a consistent solution of equations (8) and (9) when

$$\widehat{\alpha\alpha}+\widehat{\beta\beta} = \widehat{\alpha\alpha}_\phi+\widehat{\beta\beta}_\phi = \widehat{\alpha\alpha}_\psi+\widehat{\beta\beta}_\psi = 0.$$

(12) The foregoing results will be applied to the solution of a few examples.

In the case of a solid having an unlimited plane upper boundary, given by $y=0$, to determine the stresses due to normal pressure increasing uniformly as the distance from a given straight line in the plane $y=0$.

Take the axis of x in the plane $y=0$ at right angles to the given straight line, the axis of y being drawn into the solid.

Take $$\phi = \frac{P}{\pi a}\left[\frac{y}{2}\log(x^2+y^2)-x\left(\frac{\pi}{2}+\tan^{-1}\frac{x}{y}\right)\right], \tag{27}$$

and the system of stresses

$$\left.\begin{aligned}\widehat{xx} &= \phi+y\frac{\partial\phi}{\partial y} = \frac{P}{\pi a}\left[-x\left(\frac{\pi}{2}+\tan^{-1}\frac{x}{y}\right)+y\log(x^2+y^2)+y\right]\\ \widehat{yy} &= \phi-y\frac{\partial\phi}{\partial y} = \frac{P}{\pi a}\left[-x\left(\frac{\pi}{2}+\tan^{-1}\frac{x}{y}\right)-y\right]\\ \widehat{xy} &= \quad -y\frac{\partial\phi}{\partial x} = \frac{P}{\pi a}\left[\ y\left(\frac{\pi}{2}+\tan^{-1}\frac{x}{y}\right)\right]\end{aligned}\right\}. \tag{28}$$

On the plane $y=0$ there is normal pressure

$\widehat{yy} = -Px/a$, for x positive, all the rest of the surface being free.

$\widehat{xy} =$ zero everywhere on the same plane.

In this example $\theta=\tan^{-1}x/y$ is measured from the y axis.

(13) If now uniformly increasing tension is taken, commencing at the point $x = a$, and combined with the preceding, loading as shown in fig. 1 is obtained.

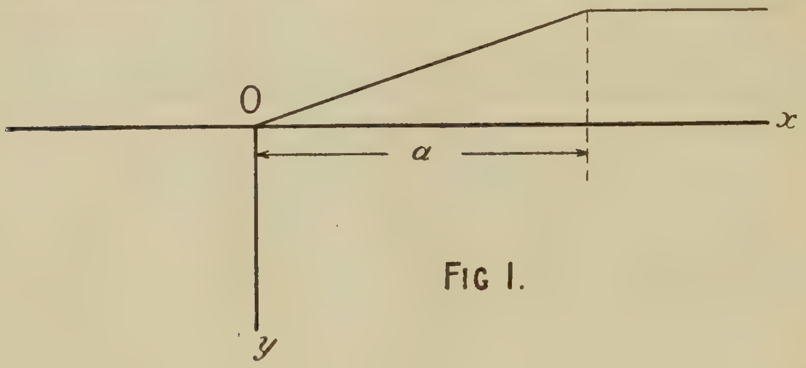

FIG I.

There is no difficulty in showing that the stresses when reduced to the same axes are as follows :—

$$\left.\begin{aligned} \widehat{xx} &= -\frac{P}{\pi a}\left[a\left(\frac{\pi}{2}+\tan^{-1}\frac{x-a}{y}\right)+x\left(\tan^{-1}\frac{x}{y}-\tan^{-1}\frac{x-a}{y}\right)\right. \\ &\qquad\qquad\qquad\qquad\qquad\qquad \left.+y\log\frac{(x-a)^2+y^2}{x^2+y^2}\right] \\ \widehat{yy} &= -\frac{P}{\pi a}\left[a\left(\frac{\pi}{2}+\tan^{-1}\frac{x-a}{y}\right)+x\left(\tan^{-1}\frac{x}{y}-\tan^{-1}\frac{x-a}{y}\right)\right] \\ \widehat{xy} &= \frac{P}{\pi a}\left[y\left(\tan^{-1}\frac{x}{y}-\tan^{-1}\frac{x-a}{y}\right)\right] \end{aligned}\right\}. \tag{29}$$

The normal stress on the plane $y = 0$ is

$\widehat{yy} = -Px/a$, for x in the interval $0 < x < a$.

$\widehat{yy} = -P$, for x in the interval $a < x < \infty$.

$\widehat{yy} =$ zero for x in the interval $-\infty < x < 0$,

and $\widehat{xy} = 0$ everywhere on the same plane.

(14) The stresses due to uniform tension P per unit of area, over one-half of an unlimited plane boundary to a solid, have been given by the stress function method,* but as the result is required in the next example, it may be permitted to obtain it by the method of the present paper.

Put
$$\phi = \frac{P}{\pi}\left(\frac{\pi}{2}+\tan^{-1}\frac{x}{y}\right), \tag{30}$$

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* 'Proc. Roy. Soc. of Edin.,' vol. 33, Part III, No. 26, p. 294.

and take the scheme of stresses

$$\left.\begin{aligned}\widehat{xx} &= \phi+y\frac{\partial\phi}{\partial y} = \frac{P}{\pi}\left[\frac{\pi}{2}+\tan^{-1}\frac{x}{y}-\frac{xy}{r^2}\right]\\ \widehat{yy} &= \phi-y\frac{\partial\phi}{\partial y} = \frac{P}{\pi}\left[\frac{\pi}{2}+\tan^{-1}\frac{x}{y}+\frac{xy}{r^2}\right]\\ \widehat{xy} &= \quad -y\frac{\partial\phi}{\partial x} = \frac{P}{\pi}\left[\qquad\qquad\qquad -\frac{y^2}{r^2}\right]\end{aligned}\right\}. \tag{31}$$

If in this case the origin is transferred to the point $x = -b$, the above stresses become

$$\left.\begin{aligned}\widehat{xx} &= \frac{P}{\pi}\left[\frac{\pi}{2}+\tan^{-1}\frac{x-b}{y}-\frac{(x-b)y}{(x-b)^2+y^2}\right]\\ \widehat{yy} &= \frac{P}{\pi}\left[\frac{\pi}{2}+\tan^{-1}\frac{x-b}{y}+\frac{(x-b)y}{(x-b)^2+y^2}\right]\\ \widehat{xy} &= \frac{P}{\pi}\left[\qquad\qquad\qquad\qquad -\frac{y^2}{(x-b)^2+y^2}\right]\end{aligned}\right\}. \tag{32}$$

These give normal tension of intensity P over the plane $y = 0$ from $x = b$ to $x = \infty$, all the remainder of the surface being free.

15. If the results of equations (29) and (32) are added together, there is obtained loading as shown in fig. 2, all the rest of the surface being free.

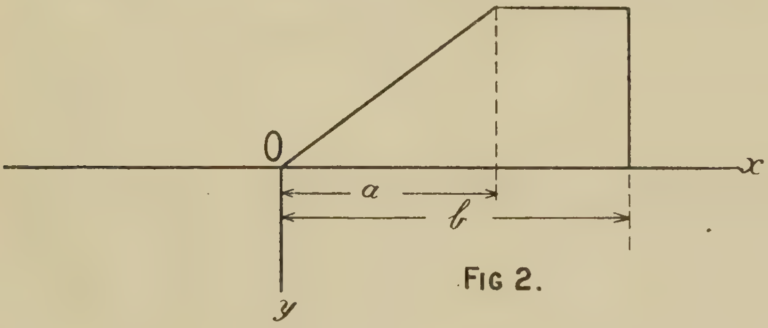

FIG 2.

The stresses due to this loading are as follows:—

$$\left.\begin{aligned}\widehat{xx} &= -\frac{P}{\pi a}\left[a\left(\tan^{-1}\frac{x-a}{y}-\tan^{-1}\frac{x-b}{y}\right)+x\left(\tan^{-1}\frac{x}{y}-\tan^{-1}\frac{x-a}{y}\right)\right.\\ &\qquad\qquad \left.+y\log\frac{(x-a)^2+y^2}{x^2+y^2}+\frac{ay(x-b)}{(x-b)^2+y^2}\right]\\ \widehat{yy} &= -\frac{P}{\pi a}\left[a\left(\tan^{-1}\frac{x-a}{y}-\tan^{-1}\frac{x-b}{y}\right)+x\left(\tan^{-1}\frac{x}{y}-\tan^{-1}\frac{x-a}{y}\right)\right.\\ &\qquad\qquad \left.-\frac{ay(x-b)}{(x-b)^2+y^2}\right]\\ \widehat{xy} &= \quad \frac{P}{\pi a}\left[y\left(\tan^{-1}\frac{x}{y}-\tan^{-1}\frac{x-a}{y}\right)-\frac{ay^2}{(x-b)^2+y^2}\right]\end{aligned}\right\}. \tag{33}$$

(16) There is no difficulty in obtaining from the foregoing the results for triangular loading of maximum intensity P as shown in fig. 3.

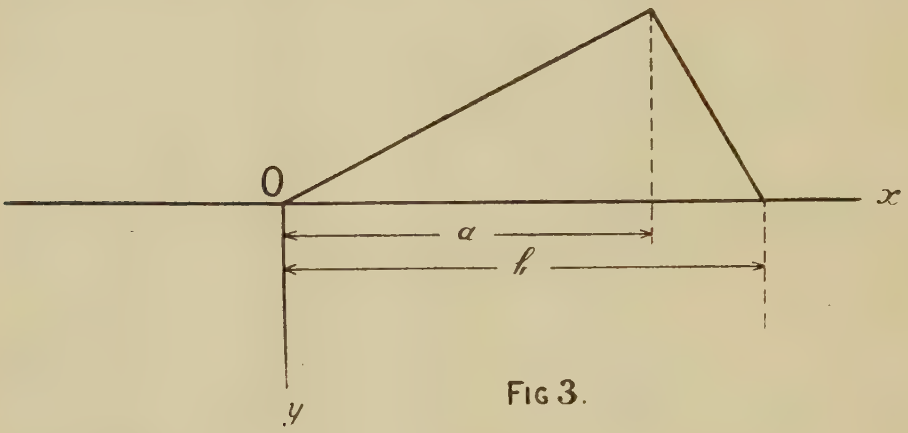

FIG 3.

The stresses are

$$\left.\begin{aligned}
\widehat{xx}=\frac{\mathrm{P}}{\pi a(b-a)}\Big[&-bx\left(\tan^{-1}\frac{x}{y}-\tan^{-1}\frac{x-a}{y}\right)+ax\left(\tan^{-1}\frac{x}{y}-\tan^{-1}\frac{x-b}{y}\right)\\
&-ab\left(\tan^{-1}\frac{x-a}{y}-\tan^{-1}\frac{x-b}{y}\right)+by\log\frac{x^2+y^2}{(x-a)^2+y^2}\\
&+ay\log\frac{(x-b)^2+y^2}{x^2+y^2}\Big]\\
\widehat{yy}=\frac{\mathrm{P}}{\pi a(b-a)}\Big[&-bx\left(\tan^{-1}\frac{x}{y}-\tan^{-1}\frac{x-a}{y}\right)+ax\left(\tan^{-1}\frac{x}{y}-\tan^{-1}\frac{x-b}{y}\right)\\
&-ab\left(\tan^{-1}\frac{x-a}{y}-\tan^{-1}\frac{x-b}{y}\right)\Big]\\
\widehat{xy}=\frac{\mathrm{P}y}{\pi a(b-a)}\Big[&b\left(\tan^{-1}\frac{x}{y}-\tan^{-1}\frac{x-a}{y}\right)-a\left(\tan^{-1}\frac{x}{y}-\tan^{-1}\frac{x-b}{y}\right)\Big]
\end{aligned}\right\}. \tag{34}$$

As these results are of some practical importance, the stresses could be expressed more simply by writing $\theta=\tan^{-1}x/y$, $\theta_1=\tan^{-1}(x-a)/y$, and $\theta_2=\tan^{-1}(x-b)/y$, where θ, θ_1, and θ_2 are measured from the planes $x=0$, $x=a$, and $x=b$ respectively, and are positive on the side on which x increases and negative on the other side.

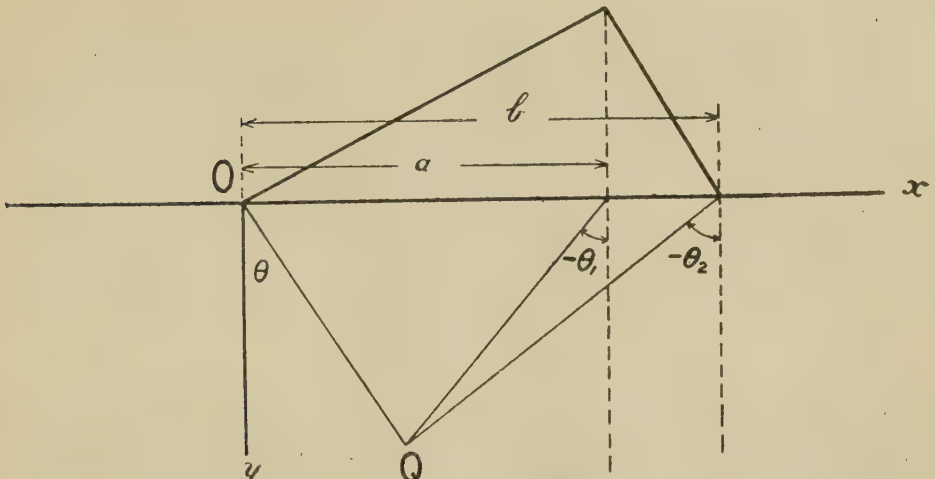

FIG 4.

The stresses at the point Q, for example, could be written thus:—

$$\left.\begin{aligned}\widehat{xx} &= \frac{\mathrm{P}}{\pi a(b-a)}\Big[-bx(\theta+\theta_1)+ax(\theta+\theta_2)-ab(\theta_2-\theta_1)\\ &\qquad\qquad +by\log\frac{x^2+y^2}{(x-a)^2+y^2}+ay\log\frac{(x-b)^2+y^2}{x^2+y^2}\Big]\\ \widehat{yy} &= \frac{\mathrm{P}}{\pi a(b-a)}[-bx(\theta+\theta_1)+ax(\theta+\theta_2)-ab(\theta_2-\theta_1)]\\ \widehat{xy} &= \frac{\mathrm{P}y}{\pi a(b-a)}[\ \ b(\theta+\theta_1)-a(\theta+\theta_2)]\end{aligned}\right\}. \qquad (35)$$

(17) The following example is of considerable theoretical interest. Consider an infinitely long slab of thickness 2π, the axis of y being in the central plane of the slab, as shown in fig. 5.

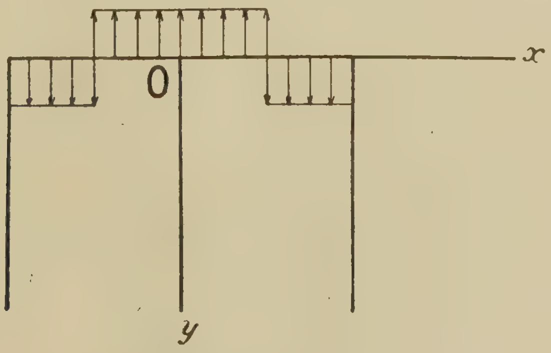

FIG 5.

If we take

$$\phi+i\psi=f(x+iy)=\tan^{-1}\frac{\cos x}{\operatorname{sh} y}+i\,\tfrac{1}{2}\log\frac{\operatorname{ch} y+\sin x}{\operatorname{ch} y-\sin x},$$

then the scheme of stresses

$$\left.\begin{aligned}\widehat{xx}&=\phi+y\frac{\partial\phi}{\partial y}-\phi\\ \widehat{yy}&=\phi-y\frac{\partial\phi}{\partial y}+\phi\\ \widehat{xy}&=\quad -y\frac{\partial\phi}{\partial x}+\psi\end{aligned}\right\}, \tag{36}$$

gives tension over the central half of the edge $y=0$ of intensity π and pressure of equal intensity over the remainder. There are certain shearing stresses on the edge $y=0$, but these are in equilibrium and may be considered as having a purely local effect.

The normal pressures and tensions on the edge $y=0$ are in equilibrium, and it will be a matter of great interest to ascertain to what depth their effect penetrates.

As the solution is of special interest, the stresses of equations (36) will be written in full and are as follows:—

$$\left.\begin{aligned}\widehat{xx}&=-\cos x\,\frac{y\operatorname{ch} y}{\operatorname{sh}^2 y+\cos^2 x}\\ \widehat{yy}&=2\tan^{-1}\frac{\cos x}{\operatorname{sh} y}+\cos x\,\frac{y\operatorname{ch} y}{\operatorname{sh}^2 y+\cos^2 x}\\ \widehat{xy}&=y\,\frac{\operatorname{sh} y\sin x}{\operatorname{sh}^2 y+\cos^2 x}+\tfrac{1}{2}\log\frac{\operatorname{ch} y+\sin x}{\operatorname{ch} y-\sin x}\end{aligned}\right\}. \tag{37}$$

There are normal tensions on the faces $x=\pm\pi$ of intensity $\widehat{xx}=y/\operatorname{ch} y$, but these can be removed by the introduction of a suitable series of stress terms, as follows:—

$$\left.\begin{aligned}-\widehat{xx}=\widehat{yy}&=a_1\sin\pi\alpha\operatorname{ch}\pi\beta+a_2\sin 2\pi\alpha\operatorname{ch}2\pi\beta+\text{etc.}\\ \widehat{xy}&=a_1\cos\pi\alpha\operatorname{sh}\pi\beta+a_2\cos 2\pi\alpha\operatorname{sh}2\pi\beta+\text{etc.}\end{aligned}\right\}, \tag{38}$$

where

$$\alpha+i\beta=\frac{\operatorname{sh} y}{\operatorname{ch} y-\cos x}+i\,\frac{\sin x}{\operatorname{ch} y-\cos x}, \tag{39}$$

$$a_m=2\int_0^1 f(\lambda)\sin m\pi\lambda\,d\lambda,$$

and

$$f(\lambda)=\frac{1-\lambda^2}{1+\lambda^2}\log\frac{1+\lambda}{1-\lambda}.$$

The coefficients can be obtained by graphical integration. It may be remarked that there is no risk that the terms in the series (38) will remove the stresses on the edge $y = 0$ at the same time as the stresses on the faces $x = \pm\pi$ are reduced to zero. To see this it is only necessary to remark that $\sin m\pi\alpha$ is everywhere zero on the edge $y = 0$ except at the single point $x = y = 0$.

It will be found that the stresses fall off in intensity as y increases with extreme rapidity, and this example affords confirmation, if such were needed, of the accuracy of the principle of equipollent loads.

(18) The function

$$\alpha_1 + i\beta_1 = f(x+iy) = \frac{\sin x}{\operatorname{ch} y + \cos x} + i\frac{\operatorname{sh} y}{\operatorname{ch} y + \cos x}, \tag{40}$$

when applied to slabs of thickness 2π, will afford interesting examples. In this case it will be easy to arrange for nuclei of stress on the edges formed by the intersection of the plane $y = 0$ and the faces $x = \pm\pi$.

For example, $\overset{\frown}{xx} = -\overset{\frown}{yy} = \beta_1$, $xy = \alpha_1$ affords such a case, and other interesting cases will present themselves.

(19) The movements corresponding to equations (10) and in the case of the examples can be calculated by the method given in Love's 'Elasticity,' 2nd edit., p. 202.

On Alternating Current Electrolysis.

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(Communicated by E. H. Griffiths, Sc.D., F.R.S. Received October 21, 1919.)

In the summer of 1915, Mr. E. Meigh, M.Sc., and the author, were engaged in some research dealing with the behaviour of bacteria under the action of electric fields. No definite conclusions were formed concerning the action of alternating electrostatic fields, and it was decided, therefore, to examine the effect of an alternating electric current on bacteria. It was noticed, however, that small bubbles of gas were formed at the electrodes, and, although these bubbles were not in the field of view of the microscope, nevertheless, they gave rise to a displacement of the volume of liquid under examination, this displacement masking completely any changes that might have occurred in the movement of the bacteria. This led to an investigation of the conditions under which such bubbles were formed, and, in the end, to a detailed examination by the author of some of the phenomena of alternating current electrolysis.

§ 1. *Introductory.*

The subject of alternating current electrolysis has been investigated by Le Blanc and Schick,* Ruer,† Brochet and Petit,‡ Maneuvrier and Chappuis,§ among others. Most of the investigations deal with the passage of alternating current through solutions of cyanides, chlorides, etc., electrodes of different metals being employed, and they are concerned principally with the question of the solution of the electrodes and the chemical changes occurring in the electrolytes. The experiments of Ruer, Brochet and Petit, and Maneuvrier and Chappuis, deserve further notice. Ruer (*loc. cit.*) used platinum electrodes in dilute sulphuric acid. Three electrodes were employed, A, B, C; alternating current was passed between A and B, and, simultaneously, a direct current was passed between C and A and B, the two latter connected together and serving as anode. He stated that platinum was not dissolved by alternating current alone, but dissolved when the electrodes between which the alternating current is passing are subjected to anodic polarisation. He suggested that, if the platinum anode is covered with a thin film of peroxide, then the hydrogen evolved in one half of a period would reduce the peroxide to the oxide, which would be readily acted upon by the acid. This view was contested by Brochet and Petit (*loc. cit.*), who maintained that the solution of the platinum is due to variation in the current density, and not to any specific action of the alternating current. According to them, a sinuoidal alternating current from a special valve gives the same effect as the combination of alternating and direct currents. Ruer criticised these experiments, and offered further evidence in support of this theory.

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* Le Blanc and Schick, 'Journ. Chem. Soc.,' vol. 2, p. 229 (1904).

† Ruer, 'Journ. Chem. Soc.,' vol. 2, p. 407 (1903).

‡ Brochet and Petit, 'Ann. Chim. Phys.,' vol. 3, p. 453 (1904).

§ Maneuvrier and Chappuis, 'Comptes Rendus,' vol. 106, pp. 499, 1719 ; vol. 107, p. 31 (1888).

Maneuvrier and Chappuis made qualitative investigations on alternating current electrolysis, dealing more especially with the effect of variation of current density and current frequency upon the production of visible electrolysis. Their results will be referred to in a later section of this paper.

§ 2. *Earlier Experiments by Meigh and Marsh.*

The electrolyte was contained in a wide tube 5 cm. diameter, fitted with three side tubes (fig. 1). Of these, X and Y were graduated burettes, while Z was a feed tube, through which electrolyte was poured into EF. The ends E and F were closed with rubber stoppers, each pierced with three holes, through which passed tubes holding the electrodes A and D,

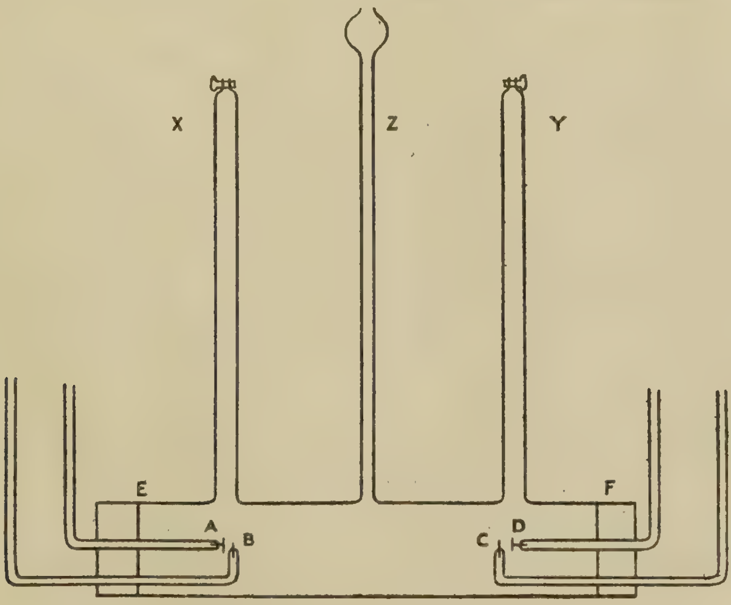


FIG 1. EF = 36 cm. AD = 20 cm.
AB = 1 cm. (approx.) CD = 0·5 cm. (approx).

explorers B and C, and also thermometers (not shown). The electrodes consisted of thin discs of platinum approximately 1 cm. diameter, which were attached to short pieces of platinum wire sealed through the ends of the tubes. These tubes were filled with mercury, and the ends of the supply leads placed in them. In order to measure the potential drop in the neighbourhood of the electrodes during the experiment, explorers were introduced. Each consisted of a very fine platinum wire, which projected about a millimetre from a fine glass tube, enclosing and thus insulating the wire (with the exception of the free end) from the liquid. Contact was made by means of mercury, as before.

Alternating current was supplied from a small Westinghouse motor generator set, giving 105 volts at 40 cycles. The tube EF was immersed in a trough, through which cold water circulated, and in this way the temperature was maintained fairly constant.

It was soon observed that the rate of gas evolution was by no means uniform, but fell off rapidly, and finally ceased altogether. Simultaneously, the platinum changed from its usual appearance to a dull black or greyish black. It appeared that this was the normal procedure with all specimens of platinum used under the conditions of the experiment.

Experiments were made with a view to the restoration of such used platinum to its original state as regards gas evolution. To this end a third electrode of platinum was introduced into EF down the tube Z, A and D were connected together, and a direct current was passed between A and D, acting as anode, and the middle electrode, which served as cathode. This direct current was allowed to pass for different times, and, after each such passage, alternating current was passed through until no further evolution of gas took place. The volume of gas given off by the alternating current was to some extent an indication of the degree of recovery of the electrode due to the passing of direct current.

During the passage of direct current, the electrodes A and D were surrounded by nascent oxygen, and it was observed that the degree of recovery of the electrodes depended in some measure upon the duration of the direct current. The actual details, and also the values of the potential distribution in the electrolyte, will be reserved for a later paragraph.

§ 3. *Later Experiments by Marsh.*

More systematic and detailed experiments have been carried out by the writer. It seemed highly probable that the phenomena would depend on the frequency of alternation, and, in order to investigate this point, a Crompton machine was used, in which the current frequency could be varied between

25 and 80 per second. The frequency was read on Frahm and Hartman and Braun meters. The current was maintained at 1 ampère throughout the series. (Transformers were used when the machine was running at low speeds, in order to supply the voltage necessary to drive a current of 1 ampère through the electrolyte.)

Several series of experiments have been carried out with apparatus similar in type to that already described; thick platinum foil, thin platinum foil, gold foil, nickel foil being used as electrodes, and dilute sulphuric acid and barium hydrate solution as electrolytes. The electrodes had practically the same area in all cases.

In carrying out a series of experiments at different frequencies, sufficient electrolyte was made for the complete set. In the case of the acid, the strength of the solution was approximately normal. The left electrode (consisting of thin platinum) was used throughout, and no evolution of gas occurred there throughout the series. Fresh acid and a fresh right electrode were used for each frequency test. The tube EF was cooled by immersion in a trough of cold water. The volumes of gas given off were reduced to 0° C. and 76 cm. of mercury pressure.

§ 4. *Experiments with Thick and Thin Platinum Foil in Dilute Sulphuric Acid.*

The curves showing the relation between the volume of gas given off and the time for different frequencies are given in fig. 2. Their striking resemblance to the saturation curves in radioactivity will be noticed, as also the outstanding effect of variation of frequency upon the total volume evolved.

Curves of similar type were obtained with thin platinum foil, the volumes given off, however, being less than in the corresponding cases with thick foil. The thicknesses of the thick and thin foils were 0·21 mm. and 0·11 mm. respectively. The volumes given off from the thin foil were approximately half those from the corresponding experiments with thick foil. Later experiments, with different thick foil, showed that although more is evolved, in general, from thick than thin foil, yet the relations between the volumes given off were not of such a simple nature as the above.

In fig. 3 are shown the relations between the total volumes liberated and the corresponding frequencies for both thick and thin foil. On plotting log volume against log frequency we get two approximately straight and parallel lines. This would represent a relation of the form $V_n \, . \, n^\beta = C$; the values of β and C for thick foil are 2·6 and $1·406 \times 10^5$ respectively; for thin foil 2·6 and $7·889 \times 10^4$.

The following Table shows the good agreement between the observed volumes and those calculated from the above formulæ.

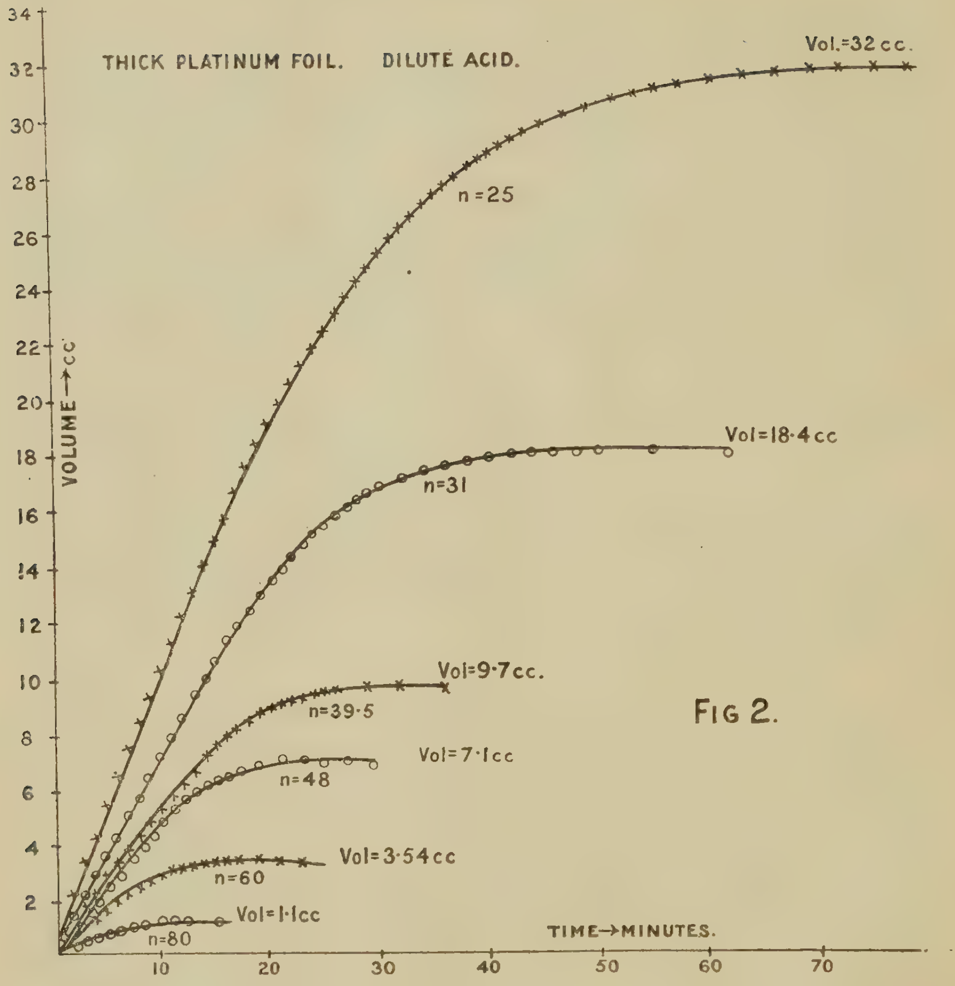


Fig 2.

Table I.

Thick Foil.			Thin Foil.		
$V_n . n^{2·6} = 1·405 \times 10^5$.			$V_n . n^{2·6} = 7·889 \times 10^4$.		
Frequency *n*.	Calculated volume.	Observed volume.	*n*.	Calculated volume.	Observed volume.
	c.c.	c.c.		c.c.	c.c.
25	32·6	32·0	25	18·28	18·1
30·5–31	18·66	18·4	30·5	10·91	10·9
39·5	9·89	9·7	39	5·75	5·6
48	5·98	7·1	48	3·36	3·6
60	3·37	3·54	60	1·89	1·8
80	1·58	1·1			

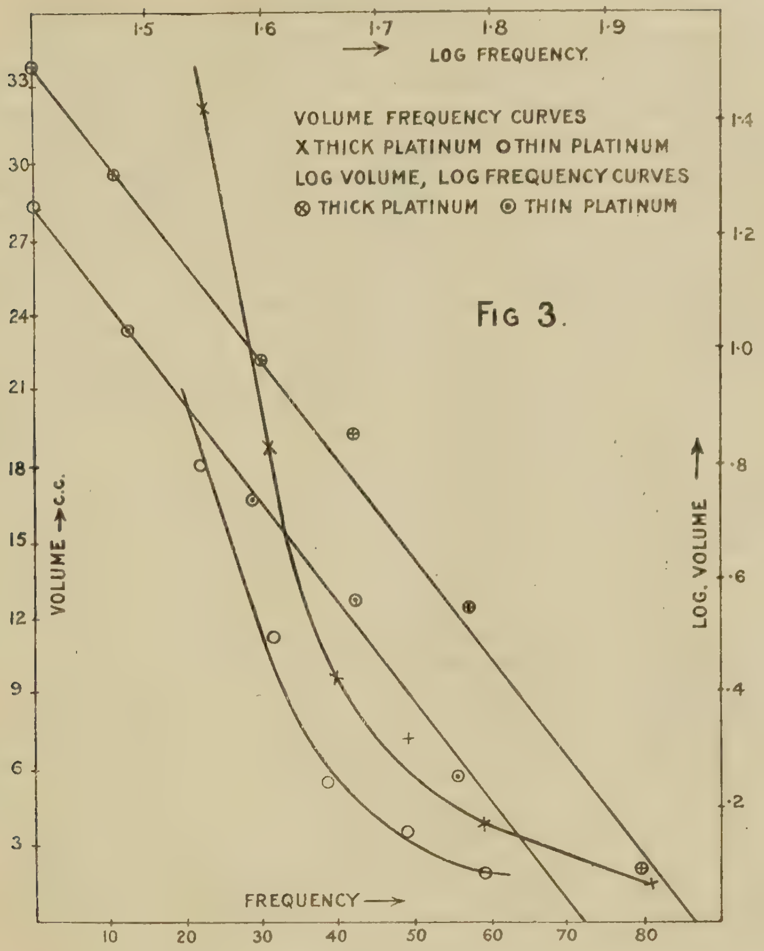


FIG 3.

§ 5. *Effect of Variation of Current Density upon Evolution of Gas.*

The machine was run at 30·5 cycles per second, and a series of experiments made with electrodes of thick platinum foil of different areas, the current being 1 ampère in each case. Four electrodes were employed, their areas decreasing approximately in geometric progression. The largest electrode was that already used at 30·5 cycles in the experiments described in § 4. As was expected, there was a much greater evolution of gas with the smaller electrodes. The following Table shows the values for the different electrodes:—

Table II.

Electrode.	Area (one face only).	Gas evolved (N.T.P.).
	sq. cm.	c.c.
I	1·298	18·4
II	0·608	58·4
III	0·323	126·2
IV	0·162	341·0 approx.

It should be noted that gas is still coming off, although in minute quantities, even although the current has passed for a long time, *e.g.*:—

With electrode II the gas evolution is 0·01 c.c. per minute after $t = 120'$.
III „ „ 0·02 „ „ „ $t = 170'$.
IV „ „ 0·05 „ „ „ $t = 470'$.

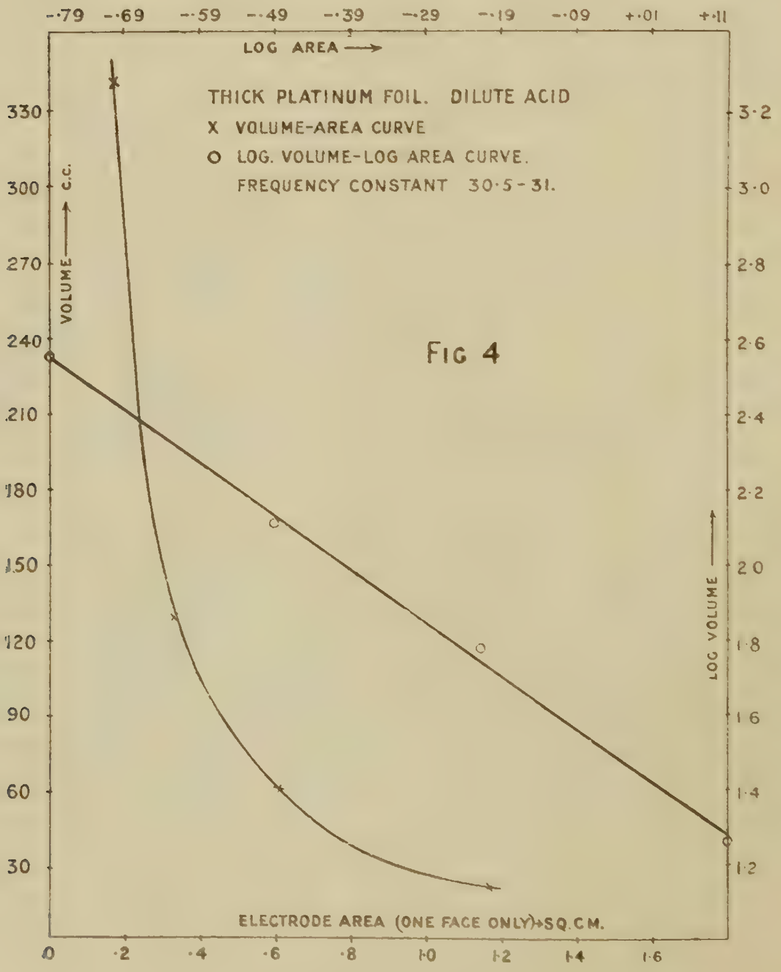


FIG 4

It will be seen from reasons advanced in § 11 that it is doubtful whether in, say, case IV, the rate of gas evolution would ever be reduced to zero, however long the current be passed.

In fig. 4 the total volume given off is plotted against the area of the electrodes, and it will be seen that the points lie very well on a smooth curve. On the same diagram, log volume is plotted against log area, and the result is approximately a straight line. The relation between volume and area is of the form $V.S^{\alpha} = b$, where S = area; $\alpha = 1{\cdot}403$, $b = 26{\cdot}55$.

An experiment was made with the *same current density*, but with a smaller

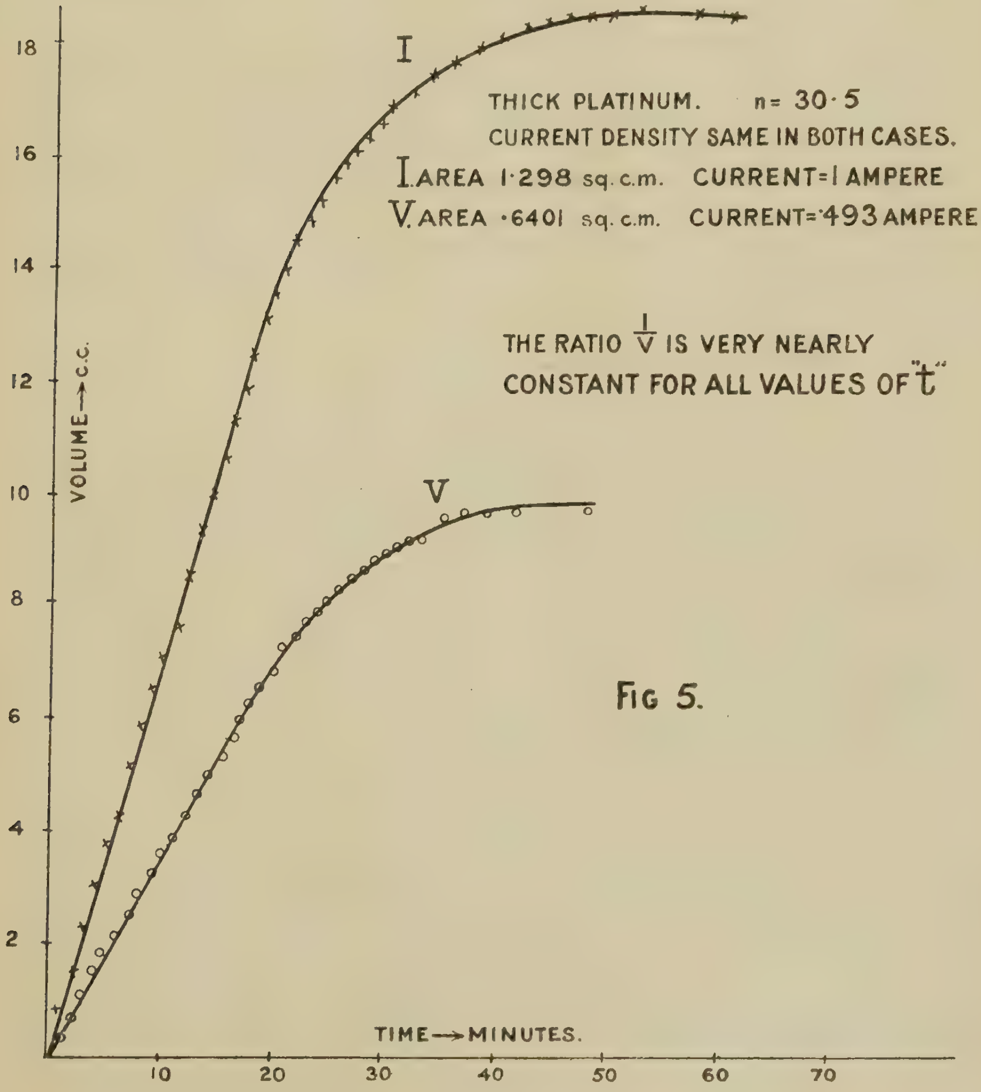


FIG 5.

electrode, the frequency being 30·5. Full details are given in the following Table and the curves shown in fig. 5:—

Table III.

Electrode.	Area (on face).	Relative areas.	Current.	Volume of gas evolved.
	sq. cm.		ampère.	c.c.
I	1·298	1	1	18·4
V	0·6401	0·4932	0·4932	9·69

The ratio between the total volumes as also between the volumes evolved at intermediate times is practically constant and approximately equal to the current ratio. Hence we infer that the actions taking place at I are occurring in the same degree and manner at V, and that for *equal* current density the *total volume* of gas liberated by an electrode is proportional to its area, frequency being constant throughout. It should be observed that the current density is not constant over the electrode, but is greatest at the edges. Hence halving, say, electrode area and current does not give exactly the same current density as before.

§ 6. *Experiments with Gold and Sulphuric Acid.*

The results of these experiments are shown in fig. 6. The rate of evolution falls off rapidly with time, but for frequencies less than 48 gas is still given off at the electrodes for a much longer time than with platinum. The volumes of gas given off are considerably smaller, in general, than in the case of platinum.

The surface of the gold becomes curiously speckled or mottled by the passage of the current.

The current density was also varied by using electrodes of different areas, the current being maintained at 1 ampère.

The results are given in the following Table:—

Table IV.

Frequency 39·5.	Full size electrode.	Half size electrode.	Quarter size electrode.
	c.c.	c.c.	c.c.
Gas evolved	5·11	16·9	82·4
Rate of evolution of gas in c.c. per minute	0·01 after $t = 50'$	0·065 after $t = 70'$	0·13 after $t = 156'$

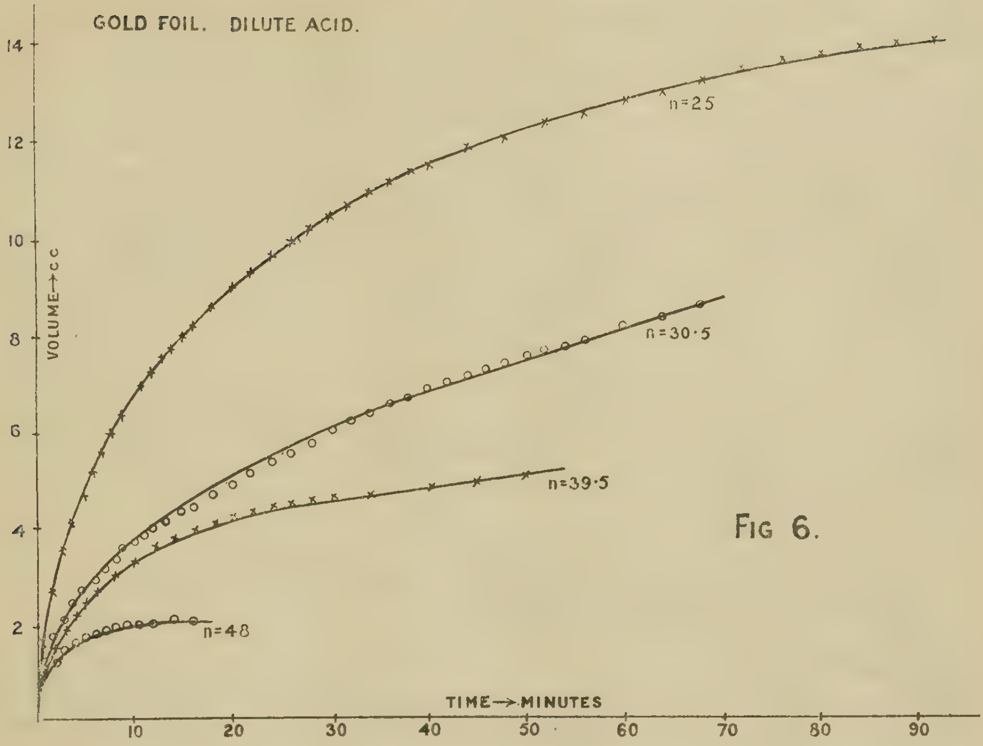


FIG 6.

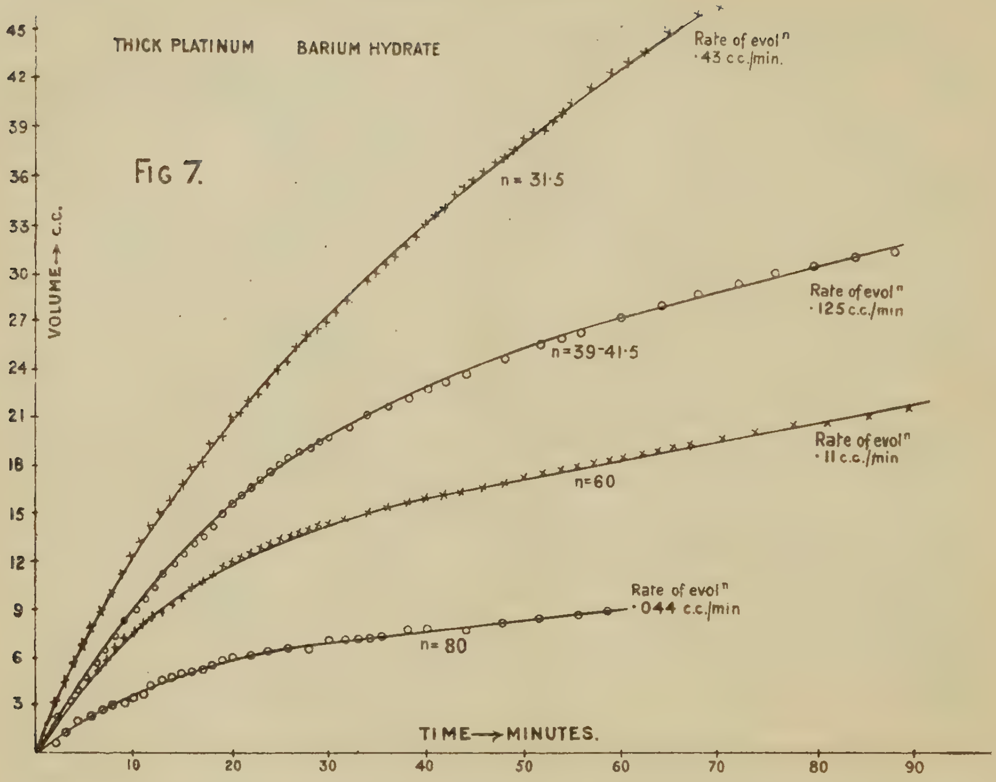
§ 7. *Experiments with Nickel and Dilute Acid.* Area 1·43 sq. cm., frequency 39·5.

A copious evolution of gas took place, the (uncorrected) rate per minute being 3·1 c.c. for the first 20 minutes, after which the electrode fell off owing to dissolving in the acid. The evolved gas was passed into the burette for absorption of oxygen, but after several days the volume had only diminished from 69·8 c.c. to 69·4 c.c. showing that there was practically no oxygen present and the gas entirely hydrogen. The theoretical rate of production of hydrogen is 3·14 c.c. per minute, which agrees remarkably well with the rate observed above.

§ 8. *Experiments with Barium Hydrate as Electrolyte.*

As somewhat complicated reactions occur when sulphuric acid is used as the electrolyte, it was thought desirable to use an electrolyte of entirely different nature.

A solution of barium hydrate of strength approximately N/10 was made up. Owing to the high specific resistance of the solution, it was necessary to use a two step-up transformer at the lower frequencies. There was considerable



heating in the tube, and this was the more marked in the case of the large machine, owing to the impossibility of maintaining a constant flow of cold water round the tube; (with the small machine it was possible to circulate water round the tube). The solution was boiled for some minutes before using, in order to drive out as much as possible of the dissolved air.

Experiments, similar in nature to those carried out with acid, were made using electrodes of gold, platinum and nickel foil. The results are shown in figs. 7 and 8.

It will be noticed that there are no signs of the flat saturation type of curve obtained when acid is used. On the contrary, the curves seem to show that, after a long period of time, gas is evolved at a steady rate, the rate decreasing with increasing frequency.

The volumes liberated in the same time are much greater with barium hydrate as electrolyte than with acid. The curves for platinum and gold are of a similar type. With nickel electrodes at a frequency of 60 cycles only the minutest bubbles were given off. On reducing the speed to 40 cycles a few more bubbles were given off, but the volume was far too small to measure.

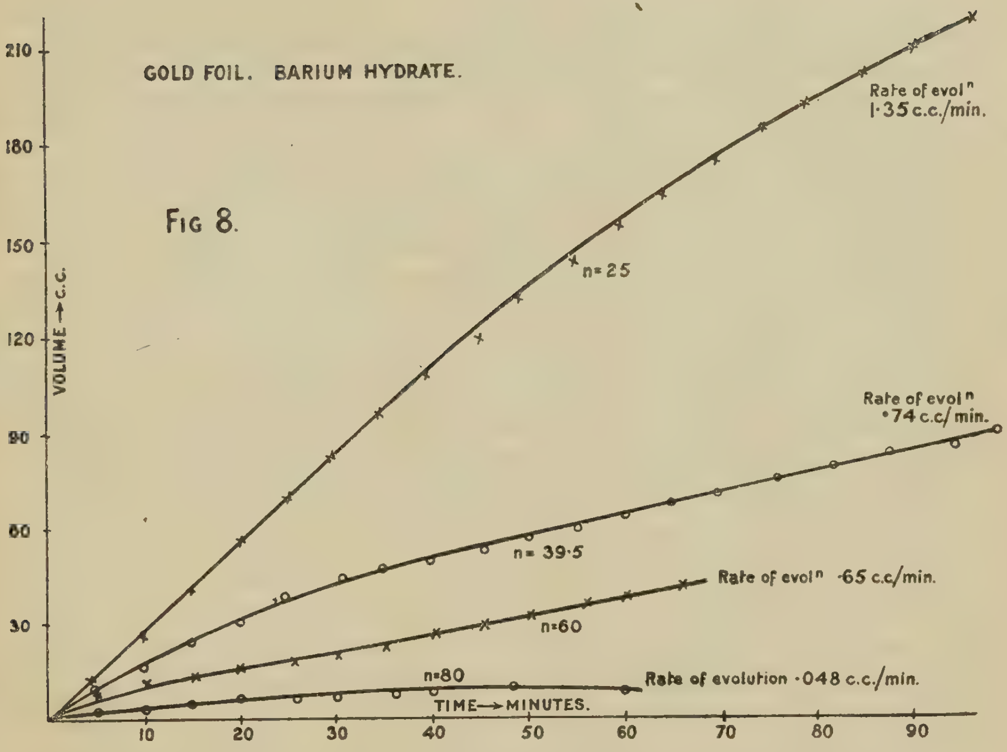


Fig 8.

§ 9. *Critical Discussion of the Results with Theoretical Suggestions.*

The effects previously described are brought about by two actions: (*a*) changes occurring at and inside the electrode, (*b*) changes taking place in the electrolyte. It is fairly easy to account in general terms for the various phenomena. There is a steady production of gas at each electrode of 4·71 c.c. per minute due to the passage of the current.

We can imagine that some of the gas liberated in any single half period is kept at the electrode and is then attacked by gas liberated in the succeeding half period, water being re-formed. Hence the total volume actually liberated per minute is considerably less than the theoretical volume.

The experiments show that in all cases the activity or power of the electrode in promoting re-combination increases with time for a definite frequency, and increases very rapidly with frequency. Now the process, in the case of platinum, may be regarded from two different standpoints:—

i. Hydrogen is easily absorbed by platinum. Hence, of the hydrogen produced in one half period at one electrode, some will escape and some will be absorbed by the electrode. Of the oxygen produced at this electrode during the succeeding half period, some will escape, some will attack the hydrogen in the electrode, re-forming water, some undoubtedly will react with the electrolyte. The re-combination may be such as to remove all the absorbed hydrogen from the electrode, although this does not appear to be very likely. In any case, the result would be a change in the quality of the surface, which would alter from a coherent compact nature to one of a porous type due to absorption and re-combination. This, in effect, would result in increased area of surface of the electrode, which would allow of increased activity both of absorption and re-combination. As a result, the rate of gas evolution would fall off very rapidly.

As a variation of the above process, it might be supposed that that portion of the hydrogen which remains at the electrode does not remain at the surface to be wholly and entirely removed by the oxygen of the succeeding half period, but diffuses into the electrode in accordance with the laws of diffusion. The curve AB in the accompanying figure, fig. 9, represents qualitatively the distribution of the hydrogen in the electrode. The oxygen is able to combine with a portion only of this hydrogen (*e.g.*, that to the left of CD, since the oxygen is not able to diffuse as quickly as hydrogen), and as a result, the electrode accumulates a store of hydrogen. The hydrogen of succeeding half periods is not able to diffuse so rapidly into the electrode, owing to the gas already present there. Hence, more and more oxygen is removed

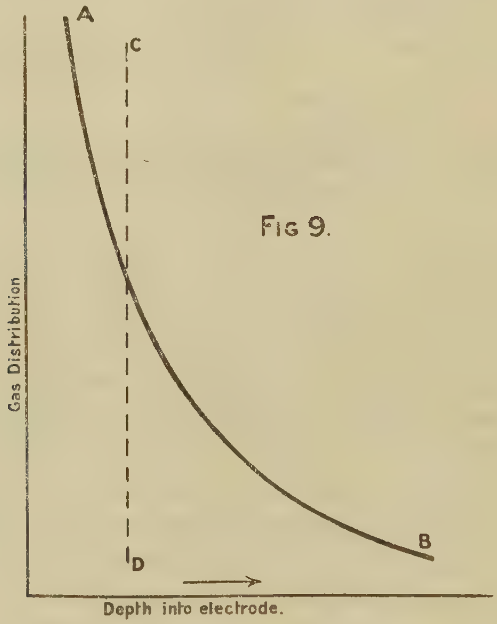


Fig 9.

by re-combination. According to this view, it would appear that oxygen would be in excess in the evolved gases. Careful tests of the composition of those gases indicate that oxygen is, if anything, in deficit. It must be pointed out, however, that the effect of the electrolyte has been ignored up to the present.

In this connection it is of interest to note the results of experiments which were carried out by Meigh and Marsh with a view to the restoration of the "used" platinum electrodes to their original state as regards evolution of gases when again employed with alternating current. These "used" electrodes were made to act as anodes with direct current for different times, and they were brought into intimate contact with active oxygen. When used subsequently as electrodes with alternating current, they permitted the evolution of gas as with new electrodes, but never to the same extent. On the other hand, such electrodes, when made to act as cathodes with direct current, do not regain this power, and no evolution of gas takes place at them when they are used subsequently with alternating current. These results seem to lend support to the theory that the inability of the electrodes to evolve gases with alternating current is due to the hydrogen which they have adsorbed and absorbed. Such hydrogen would be removed, in part, at any rate, when the electrode is made to act as anode with direct current.

ii. The process may, however, be regarded as taking place in a different manner. We may conceive of *chemical* changes occurring at the electrodes during the passage of the alternating current. The electrode may get oxidised to some oxide of platinum by the oxygen of one-half period, this oxide being reduced to a lower oxide or to the metal itself by the hydrogen of the succeeding half-period. Such oxidation and reduction would alter the constitution of the surface, making it of a more porous nature, thus exposing a greater area to the subsequent oxidising and reducing actions.

The experiments on gold and nickel may throw light upon this point. When gold electrodes (which have been used already with alternating current) are made to serve as anodes with direct current, the electrolyte being dilute acid, they recover (partially) their ability to evolve gases with alternating current. During the passage of the direct current the cathode became brighter, while a dark stain, with traces of red, appeared round the edges of the anode. (Both electrodes initially had the mottled appearance already remarked upon.) When this *direct* current is suddenly *reversed* in direction, bubbles are given off at once at that electrode which had previously acted as cathode, while at the other electrode (viz., that serving previously as the anode) no evolution of gas took place for several seconds—in one case 25 seconds, in another 8½ seconds. Colour changes also took place. The electrode acting now as anode became brown, while the other changed from reddish brown to a lighter, almost greenish, shade. These alterations of colour are probably indicative of chemical changes at the surface of the electrode. The metal is oxidised at the anode, and, on subsequent reversal of the direct current, this oxide is reduced to a lower oxide or to the metal, by the hydrogen. Until this action is complete, no gas is evolved at the electrode.

With nickel, the results are of a different nature. When nickel electrodes are used in dilute acid with direct current, then, if the current is small enough, no evolution of gas occurs at the anode, while there is a steady production of gas at the cathode. The latter remains bright, while the former becomes dull. On *reversal* of the direct current, gas is evolved at once at the *new cathode*. In this case the nickel oxidises, but the oxide formed is very soluble in acid, so that, on reversal, there is no oxide remaining for reduction by the hydrogen. This explains at once the effect observed when nickel is used with alternating current in dilute acid. The oxygen of one-half period oxidises the nickel, and the oxide thus formed dissolves in the acid. Hence little, if any, of the hydrogen is used for reducing purposes, and the evolution of the hydrogen is quite regular, and agrees with the theoretical value.

The gold oxide formed is not soluble in the dilute acid, and hence reduction takes place.

Striking changes occur when nickel electrodes are used in barium hydrate solution with direct current. When a small current is employed, bubbles are given off at the cathode only. Dark streaks and dark-coloured edges appear at the anode, and, with time, a greenish deposit forms on the anode. On reversing the current, the dark stain appears very quickly on that electrode previously serving as cathode, and is soon followed by the green deposit. It should be remarked that the dark stain spreads much more rapidly over the electrode when this has just previously been acting as cathode. The dark stain on the nickel dissolves at once in dilute sulphuric acid; the stain on the gold, when used with barium hydrate, does not dissolve in this acid.

It would appear from these facts that, in the case of gold and nickel, there is little doubt but that oxidation occurs in the process of electrolysis.

Further evidence in support of the "oxidation and reduction" theory is obtained from experiments made by Maneuvrier and Chappuis. They observed that, when copper electrodes were used with dilute sulphuric acid, and alternating current passed, no visible electrolysis set in. The electrodes became covered with a coating of red reduced copper, caused by oxidation by the ozonised oxygen, coupled with subsequent reduction by hydrogen. Using mercury electrodes, of large surface, they discovered that a small volume only of gas is evolved (nearly all hydrogen), and that a cloud of white matter is produced, which spreads gradually through the electrolyte. They showed this to be the sulphate of the protoxide.

We have next to consider whether the oxidation theory is capable of explaining (*a*) the different volumes of gases liberated at different frequencies; (*b*) the partial recovery of the electrode when made to act as anode in direct current electrolysis.

In the latter case, we may suppose that the surface of the metal gets oxidised, and, further, that this oxidised film becomes more and more coherent the greater the duration of this electrolysis. The speed of the reducing action of the hydrogen on this film will depend very much on the surface state of the latter, being greater when this film is of a porous nature. Hence, with subsequent alternating current, the efficiency of the reducing action is small at the start, and for some time evolution of gases occurs at the electrode.

An explanation of the frequency effect can be offered on the same general grounds. At high frequency, the oxidising action in one-half period persists for a short time only. The film formed is not of a close texture, and is readily reduced by the hydrogen in the succeeding half-period. With low frequencies, on the other hand, the oxidation period is longer, the film formed is more coherent and massive, and the reducing action not so speedy.

A study of the curves for gold and platinum shows that the same general tendencies are present in both cases. One would be led to infer that oxidation must play an important part in the case of platinum. Again, if the used electrodes, gold and platinum, be strongly heated, they recover partially their ability to give off gases when used with alternating current. The gold electrodes, on heating, became quite bright, while the platinum changed from greyish black to a dull silver colour. The films of oxide would break up on heating, giving a pure metal surface.

With regard to the oxidation of platinum, several investigations may be quoted. The experiments of Ruer (*loc. cit.*) have already been alluded to. The experiments of Mond, Ramsay, and Shields,* on the absorption of oxygen (and hydrogen) by platinum black, point to the formation of $Pt(OH)_2$, since the heat of occlusion of the oxygen is the same as the heat of formation of $Pt(OH)_2$.

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* Mond, Ramsay and Shields, 'Roy. Soc. Proc.,' vol. 58, p. 242 (1895); vol. 62, p. 50 (1897).

Newberry,* in a series of measurements of cathodic and anodic over-voltages of different metals in acid and alkaline electrolytes, suggests that anodic over-voltage is due to the formation of higher oxides on the surface of the electrodes, such oxides being only stable under the influence of the great pressure set up in the electrolysis.

It is not at all improbable that the *two processes of occlusion and oxidation*, which have been outlined in the preceding pages, may be taking place *simultaneously* in the experiments which have been described.

In fact, Mond, Ramsay, and Shields showed that platinum black, which had absorbed 100 volumes of oxygen, was able to absorb 310 volumes of hydrogen, 200 of which combined with the oxygen, the remainder being occluded. They concluded that, in platinum black, a certain amount of occluded oxygen could co-exist with occluded hydrogen.

It would not be unreasonable to suppose that occlusion would play a more prominent part in the case of platinum than with gold or nickel, but one is led to believe that oxidation also plays an important rôle in these experiments.

§10. *Influence of the Electrolyte upon the Phenomena.*

It is evident that the nature of the electrolyte plays an important part in these experiments. With the current densities employed there was no trace, when barium hydrate was used as the electrolyte, of the flat "saturation type" of curve obtained when sulphuric acid served as the electrolyte. The activity of the electrode is much less in barium hydrate than in acid.

One noteworthy fact deserves mention. If the mixed gases produced by electrolysis of the acid are allowed to stand for some time in the tubes over the acid, it is found that the volume diminishes by a considerable amount. With barium hydrate, on the other hand, there is little or no change of volume.

It will be seen that when $Ba(OH)_2$ is the electrolyte, there is a much greater evolution of gas with gold electrodes than with platinum electrodes. With acid, on the other hand, the opposite is the case. Further, a variation in the current density had a very marked effect on the volume of gas liberated.

Gold electrode and $Ba(OH)_2$. Current frequency 60.

Current 1·0 ampère, rate of evolution per minute 0·80 c.c.
" 1·5 " " " 1·75 c.c.
" 1·8 " " " 2·5 c.c.

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* Newberry, 'Journ. Chem. Soc. Trans.,' p. 1420 (1914); p. 1051 (1916).

§ 11. *Activity of the Electrode.*

It has been noted earlier that in no case is the theoretical quantity of gas evolved at an electrode, even at the commencement of electrolysis. Each electrode has, per unit area, a certain power of promoting re-combination of the gases $t = o'$, this power increasing with the frequency of alternation. Furthermore, this power increases with the time of passage of the current until finally, with platinum and acid, and in some cases with gold and acid, the activity of the electrode becomes so great that no further evolution of gas occurs. It appears from an analysis of the results that this activity can increase to a maximum per unit of area, the value of the maximum increasing with frequency. If the current density is less than that which would call forth the maximum activity of the electrode, then sooner or later the evolution of gas will cease. If, on the other hand, the current density is higher than that corresponding to maximum activity, then the gas after a considerable time will continue to come off, but at a uniform rate. Figs. 2 and 7 show these differences very clearly. The current density with platinum and sulphuric acid was less than that which would call forth the maximum activity, and so the curves soon run horizontally; but the current density with platinum and barium hydrate was greater than that representing the maximum activity, and as a result the curves become straight lines whose slopes decrease with increasing frequencies.

Maneuvrier and Chappuis made qualitative experiments on alternating current electrolysis, and came to somewhat similar conclusions regarding the activity of the electrodes. They did not observe, however, the important fact that for a given metal and frequency the activity is a function of the time.

§ 12. *Initial Activity of Different Electrodes.*

A few experiments were made on the initial activity of different electrodes. The machine was run at a definite speed and the current gradually increased until visible electrolysis set in.

Frequency 41·5.—With two pieces of new thin platinum foil of the same area as that previously employed, the critical initial currents for acid and $Ba(OH)_2$ respectively were 0·29 ampère and 0·1 ampère, indicating a much higher activity on the part of the electrode when in acid than when in hydrate. With gold (heated after use with alternating current) in $Ba(OH)_2$, bubbles were evolved with a current of 0·18 ampère (frequency 40·5, area same as platinum).

Nickel and Barium Hydrate.—Fine nickel wire was employed. Bubbles were given off freely when little of the wire was inserted in the hydrate. The bubbles ceased when 16 cm. of wire (diameter 0·21 mm.) were immersed; current 0·16 ampère. In another experiment the current was kept at 0·10 ampère and bubbling ceased when 10 cm. of wire were immersed. Both these give an initial activity corresponding to 0·15 ampère per square centimetre. With nickel foil and barium hydrate a current 0·24 ampère was just able to give bubbles with foil 2·7 cm. long and 2 mm. wide; in another experiment 0·36 ampère was the value for foil 4 cm. long and 2 mm. wide. Both these give an initial activity of about 0·44 ampère per square centimetre.

§ 13. *Effect of Thickness of Electrodes upon the Phenomena.*

Attention has been drawn (p. 127, § 4) to the striking results obtained with thick and thin platinum in dilute acid. At all the frequencies used, approximately twice as much gas was evolved from the thick as from the thin platinum, the ratio of the thicknesses also being as 2 : 1. In general, more gas is evolved from a thick electrode than from a thin one. It would be highly interesting to determine the relation between the volume of gas given off and the thickness of the electrode (particularly with very thin films) and the author intends to investigate this point by depositing such thin films of varying thickness upon glass.

It would appear that the activity of a thin film is greater than for a thick film of the same area. There is no doubt that the difference in the activity of the two specimens of foil depends, in part, upon the nature of their surfaces, but nevertheless one must infer that the activity is a function of the thickness also.

One may picture the process as taking place somewhat as follows:—Supposing that one of the causes of the activity is the presence of gas in the external portions of the electrode, then the greater the amount of gas present

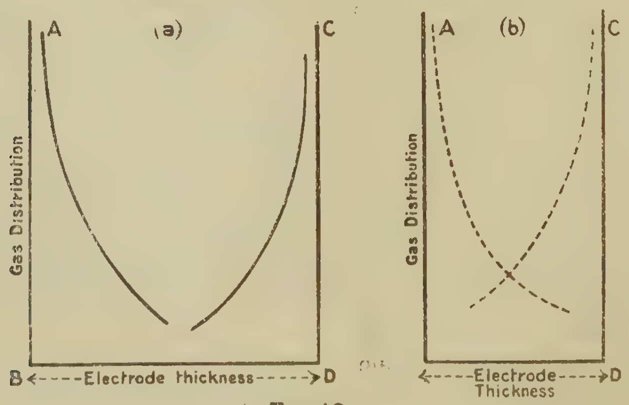

FIG 10.

at and near the face of the electrode, the greater will be the activity. Now there will be a tendency for the gases to diffuse inwards, and the rate of such diffusion will be the greater when the amount of gas present in the interior is small. In fig. 10*a* we have the case of a thick electrode where the diffusion of gas into the electrode from the face AB is unaffected by that from CD. In fig. 10*b*, on the other hand, the diffusion through one face is evidently affected by the presence of gas in the interior of the electrode, due to diffusion through the opposite face.

The gas density in the interior of the thin film is higher than that in the thick film, hence the rate of diffusion is slower in the case of the thin film than in that of the thick. In other words, there will be a greater surface activity with thin films than with thick.

§ 14. *Gas Tests.*

In most of the later experiments, the constitution of the evolved gases was determined. In some cases the oxygen was absorbed by pyrogallic acid, in others by a solution of sodium hydro-sulphite and sodium hydrate. The hydrogen present was determined by admixture with air, followed by explosion in an explosion chamber.

The general result was that the hydrogen was slightly in excess of the volume necessary to combine with the oxygen. In every case the sum of the separate volumes was slightly less (1 c.c. or so) than the volume of mixed gas.

It will be advisable in future work to carry out gas tests during the *progress* of an experiment, and not alone at the end of the experiment. The difficulty will be that of dealing with the small quantities of gas evolved.

§ 15. *Partial Restoration of Electrodes to their Original State as Regards Gas Evolution.*

If the platinum electrodes used in the acid electrolyte with alternating current are made to act as anodes with *direct current* they recover their ability to evolve gases when used again with alternating current. During the passage of the direct current, the surface of the electrodes changes from greyish-black to dull grey. The restoration is never perfect. The longer the time of passage of direct current, the greater is the volume of gas evolved subsequently by alternating current, but there appears to be no simple relation between the two quantities. If the electrodes after use with alternating current are strongly heated, they recover, in part, this power of evolving gases.

Similar effects have been observed with gold. It may be restored partially by (*a*) making it serve as the anode with direct current, (*b*) strong heating, (*c*) immersion for a short time in *aqua regia*. In the two latter operations, the mottled appearance of the gold changes immediately to the bright yellow colour of the unused foil.

In the case of barium hydrate it was observed that the ability to evolve gases was restored (in part) by giving the electrodes a rest while in the electrolyte. With sulphuric acid this was not the case—merely leaving the electrodes for some time was not efficacious in restoring them.

There are marked differences in the surface changes produced in the electrodes when in different electrolytes. On platinum in acid a greyish-black stain was produced, which could be easily wiped off. With barium hydrate, on the other hand, the stain was much blacker, particularly round the edges, and was much more adherent. Strong heating had little effect upon it.

Conclusion.

In the preceding pages the behaviour of platinum, gold and nickel electrodes during the passage of alternating current through different electrolytes has been examined. Two suggestions have been put forward to explain the phenomena: (*a*) the oxidation of the electrode, coupled with subsequent reduction by the hydrogen of the next half-period, (*b*) the absorption and adsorption of hydrogen by the electrode coupled with re-combination with oxygen of the next half-period. These processes are not mutually exclusive, and it is possible that both agencies are operative in degrees varying with the metal employed.

Further experiments with other electrodes and electrolytes (in which also the concentration is varied) are desirable.

The author hopes to resume work in some of the points outlined in the paper at an early date.

The preceding research has been carried out in the Physics Department of Battersea Polytechnic, and the author desires to take this opportunity of expressing his thanks and indebtedness to his colleagues, Mr. Wilson and Dr. White of the Chemical Department, and Mr. Thomson, late head of Physics Department, for their interest and valued criticisms during its progress. He is also indebted to Dr. E. H. Griffiths, F.R.S., for his valuable advice and suggestions during the writing of the paper.

Note on the Central Differential Equation in the Relativity Theory of Gravitation.

By Prof. A. R. FORSYTH, F.R.S., Imperial College, South Kensington.

(Received March 4, 1920.)

The critical equation in Prof. Einstein's relativity theory of gravitation is given in the form*

$$\left(\frac{du}{d\phi}\right)^2+u^2=\frac{c^2-1}{h^2}+\frac{2mu}{h^2}+2mu^3,$$

where m is the mass of the sun, u is the reciprocal of the distance of the moving body from the sun,

$$h^2=ma(1-e^2), \qquad c^2-1=-m/a,$$

a is the "major semi-axis of the orbit," the units being astronomical, and e is the "excentricity" of the orbit.

The foregoing equation can be integrated exactly, the functions involved being elliptic and not circular; and the approximations for the solar system are easily obtained, because the modulus of the elliptic functions is small. The necessary analysis is as follows.

1. The equation is

$$\left(\frac{du}{d\phi}\right)^2=-\frac{m}{ah^2}+2\frac{m}{h^2}u-u^2+2mu^3$$

$$=\mathrm{A}u^3+3\mathrm{B}u^2+3\mathrm{C}u+\mathrm{D}=\mathrm{U},$$

where $\quad \mathrm{A}=2m, \qquad \mathrm{B}=-\frac{1}{3}, \qquad \mathrm{C}=\frac{2}{3}\frac{m}{h^2}, \qquad \mathrm{D}=-\frac{m}{ah^2}.$

The equation $\mathrm{U}=0$ has three roots; and their character, as to reality, depends upon the sign of $\mathrm{G}^2+4\mathrm{H}^3$, where (with the usual notation)

$$\mathrm{H}=\mathrm{AC}-\mathrm{B}^2=-\frac{1}{9}+\frac{4}{3}\frac{m^2}{h^2},$$

$$\mathrm{G}=\mathrm{A}^2\mathrm{D}-3\mathrm{ABC}+2\mathrm{B}^3=-\frac{2}{27}+\frac{4}{3}\frac{m^2}{h^2}-4\frac{m}{ah^2}.$$

On substitution and reduction, we have

$$\mathrm{G}^2+4\mathrm{H}^3=\frac{16}{27}\frac{m^3}{ah^2}-\frac{16}{27}\frac{m^4}{h^4}-\frac{32m^5}{3ah^4}+\frac{16m^6}{a^2h^4}+\frac{256}{27}\frac{m^6}{h^6}$$

$$=\frac{m^2}{h^2}\left\{-\frac{16}{27}\frac{m^2}{h^2}+\frac{16}{27}\frac{m}{a}-\frac{32}{3}\frac{m}{a}\frac{m^2}{h^2}+16\frac{m^2}{a^2}\frac{m^2}{h^2}+\frac{256}{27}\frac{m^6}{a^6}\right\}.$$

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* Prof. Eddington's 'Report on the Relativity Theory of Gravitation,' 2nd edition, p. 50 (1920).

By using the relation

$$h^2 = ma(1-e^2),$$

the last expression leads to the equation

$$G^2+4H^3 = \frac{m^4}{h^4}\left\{-\frac{16}{27}e^2+\left(\frac{400}{27}-\frac{64}{3}e^2+16e^4\right)\frac{m^4}{h^4}\right\}.$$

In the solar system, as regards even the nearest known planets, m^2/h^2 is of the order 10^{-8}, while e^2 is never of so small an order; consequently, the first term within the bracket governs the sign of G^2+4H^3. Thus G^2+4H^3 is negative, but not attaining a limit zero within the system; therefore, by the usual rule, the three roots of $U = 0$ are real, and no two of them are equal. Let them be denoted by α, β, γ, arranged in descending order of magnitude; their product is $1/2ah^2$, a positive quantity; hence either all three real roots must be positive, or one of them must be positive and the other two must be negative.

2. As a matter of fact, the three roots are positive for the solar system. Let

$$Au+B = t;$$

then

$$t^3+3Ht+G = 0.$$

Comparing this equation, as usual when the three roots are real, with the equation

$$\cos^3\theta-\tfrac{3}{4}\cos\theta-\tfrac{1}{4}\cos 3\theta = 0,$$

we find

$$t = 2(-H)^{\frac{1}{2}}\cos\theta,$$

where

$$\cos 3\theta = -\tfrac{1}{2}\frac{G}{(-H^3)^{\frac{1}{2}}},$$

giving a positive value for $\cos 3\theta$. We shall assume a positive value for 3θ, between 0 and $\tfrac{1}{2}\pi$; there is no loss of generality in the assumption. The three values of t correspond to the values θ, $\theta+\tfrac{2}{3}\pi$, $\theta+\tfrac{4}{3}\pi$; hence, as

$$\cos(\theta+\tfrac{2}{3}\pi) = -\tfrac{1}{2}\cos\theta-\frac{\sqrt{3}}{2}\sin\theta,$$

$$\cos(\theta+\tfrac{4}{3}\pi) = -\tfrac{1}{2}\cos\theta+\frac{\sqrt{3}}{2}\sin\theta,$$

we have

$$2m\alpha-\tfrac{1}{3} = 2(-H)^{\frac{1}{2}}\cos\theta,$$

$$2m\beta-\tfrac{1}{3} = 2(-H)^{\frac{1}{2}}\cos(\theta+\tfrac{4}{3}\pi),$$

$$2m\gamma-\tfrac{1}{3} = 2(-H)^{\frac{1}{2}}\cos(\theta+\tfrac{2}{3}\pi).$$

Again,

$$\sin^2 3\theta = 1+\frac{G^2}{4H^3} = 108\,\frac{m^4e^2}{h^4}$$

approximately, for the solar system; so that

$$\theta = 2\sqrt{3}\,\frac{m^2 e}{h^2}$$

approximately. Also, approximately,

$$(-\mathrm{H})^{\frac{1}{2}} = \tfrac{1}{3} - 2\,\frac{m^2}{h^2};$$

and therefore

$$2m\beta - \tfrac{1}{3} = 2\left(\tfrac{1}{3} - 2\,\frac{m^2}{h^2}\right)\left(-\tfrac{1}{2} + \frac{\sqrt{3}}{2}\,\theta\right)$$

$$= -\tfrac{1}{3} + 2\,\frac{m^2}{h^2} + \frac{\theta}{\sqrt{3}},$$

approximately. Thus β is positive. Consequently γ is positive, and its value is given by

$$2m\gamma - \tfrac{1}{3} = -\tfrac{1}{3} + 2\,\frac{m^2}{h^2} - \frac{\theta}{\sqrt{3}}.$$

3. Returning now to the original differential equation, we have

$$\frac{du}{d\phi} = \pm \mathrm{U}^{\frac{1}{2}}$$

$$= \pm\{2m(u-\alpha)(u-\beta)(u-\gamma)\}^{\frac{1}{2}}.$$

Now $du/d\phi$ is real. For the solar system, $2m\alpha$ is approximately equal to 1, while $m = 1{\cdot}47$, and u is of order not higher than 10^{-8}. Hence

$$\beta \geqq u \geqq \gamma,$$

β being the value of u at perihelion. We shall assume that ϕ is measured positively throughout the orbit, so that $d\phi$ is positive. From perihelion to aphelion u decreases, so that du is negative in this range. Thus $du/d\phi$ is negative, and therefore

$$\frac{du}{d\phi} = -\{2m(u-\alpha)(u-\beta)(u-\gamma)\}^{\frac{1}{2}}.$$

Substitute

$$u = \gamma + (\beta-\gamma)\sin^2\psi;$$

after a slight reduction, we find

$$d\phi = -2\rho\,\frac{d\psi}{(1-k^2\sin^2\psi)^{\frac{1}{2}}},$$

where $$\rho = \{2m(\alpha-\gamma)\}^{-\frac{1}{2}}, \qquad k^2 = \frac{\beta-\gamma}{\alpha-\gamma}.$$

The value of u at perihelion is β, and it subsequently decreases; hence the value of ψ at perihelion is $\frac{1}{2}\pi$, and it subsequently decreases. Consequently, at any place before aphelion in the orbit, we have

$$\begin{aligned}\frac{\phi-\varpi}{2\rho} &= -\int_{\frac{1}{2}\pi}^{\psi}\frac{d\psi}{(1-k^2\sin^2\psi)^{\frac{1}{2}}}\\ &= \int_{\psi}^{\frac{1}{2}\pi}\frac{d\psi}{(1-k^2\sin^2\psi)^{\frac{1}{2}}}\\ &= \int_{0}^{\frac{1}{2}\pi}\frac{d\psi}{(1-k^2\sin^2\psi)^{\frac{1}{2}}}-\int_{0}^{\psi}\frac{d\psi}{(1-k^2\sin^2\psi)^{\frac{1}{2}}}\\ &= \mathrm{K}-\mu,\end{aligned}$$

where $\phi=\varpi$ at perihelion, and, in the usual notation of elliptic functions, K is the complete elliptic integral of the first kind, and

$$\psi = am\,\mu,$$

that is,

$$\psi = am\left(\mathrm{K}-\frac{\phi-\varpi}{2\rho}\right).$$

Now

$$\begin{aligned}u &= \gamma+(\beta-\gamma)\sin^2\psi\\ &= \gamma+(\beta-\gamma)\,sn^2\,\mu\\ &= \gamma+(\beta-\gamma)\,\frac{1-cn\,2\mu}{1+dn\,2\mu}\\ &= \gamma+(\beta-\gamma)\,\frac{1-cn\left(2\mathrm{K}-\dfrac{\phi-\varpi}{\rho}\right)}{1+dn\left(2\mathrm{K}-\dfrac{\phi-\varpi}{\rho}\right)}\\ &= \gamma+(\beta-\gamma)\,\frac{1+cn\,\dfrac{\phi-\varpi}{\rho}}{1+dn\,\dfrac{\phi-\varpi}{\rho}},\end{aligned}$$

which is the accurate equation of the orbit represented by the original differential equation. It involves elliptic functions, instead of the circular functions that occur in the equation of the Newtonian orbit.

4. Further, the value of ψ (decreasing from $\frac{1}{2}\pi$ at perihelion) is zero at aphelion; so, if ϕ_1 denote the value of ϕ at aphelion, we have

$$\phi_1-\varpi = 2\rho\mathrm{K}.$$

From aphelion to perihelion we have similar relations; so that, if at the next perihelion, ϕ_2 be the value of ϕ, which is to begin with ϕ_1 at aphelion, we have

$$\phi_2-\phi_1 = 2\rho\mathrm{K}.$$

Thus

$$\phi_2-\varpi = 4\rho\mathrm{K}.$$

Let the advance of the perihelion in one revolution be denoted by Δ; then

$$\Delta = (\phi_2 - \varpi) - 2\pi = 4\rho\mathrm{K} - 2\pi.$$

The expression is accurate, and not merely approximate, in connection with the original differential equation so long as the magnitudes in that equation allow three real roots for $\mathrm{U} = 0$, whatever be the gravitational system.

The preceding results are accurate, and not merely approximate, subject to the condition just stated. In the exposition of the application to the solar system, and specially with reference to the advance of the perihelion of Mercury in one complete revolution, approximation is made with regard to the magnitudes of the solar system that are involved. To bring the approximation into relation with the foregoing accurate results, we must deal with the two relations

$$u = \gamma + (\beta - \gamma)\frac{1 + cn\,\dfrac{\phi - \varpi}{\rho}}{1 + dn\,\dfrac{\phi - \varpi}{\rho}}, \qquad \Delta = 4\rho\mathrm{K} - 2\pi.$$

5. As regards the approximation to Δ, we require the most important terms in ρ and in K.

The value of ρ is

$$\{2m(\alpha - \gamma)\}^{-\frac{1}{2}}.$$

From the foregoing values of α, β, γ, we have

$$\begin{aligned} 2m(\alpha - \gamma) &= 2(-\mathrm{H})^{\frac{1}{2}}\{\cos\theta - \cos(\theta + \tfrac{2}{3}\pi)\} \\ &= 2(-\mathrm{H})^{\frac{1}{2}}\left(\frac{3}{2}\cos\theta + \frac{\sqrt{3}}{2}\sin\theta\right) \\ &= \frac{2}{3}\left(1 - 6\frac{m^2}{h^2}\right)\frac{3}{2}\left(1 + \frac{\theta}{\sqrt{3}}\right) \\ &= 1 + \frac{\theta}{\sqrt{3}} - 6\frac{m^2}{h^2}, \end{aligned}$$

to the order of approximation that includes m^2/h^2 but no higher power of m/h. Hence, to this order,

$$\begin{aligned} \rho &= 1 + 3\frac{m^2}{h^2} - \frac{1}{2\sqrt{3}}\theta \\ &= 1 + 3\frac{m^2}{h^2} - \frac{m^2 e}{h^2}. \end{aligned}$$

The value of k^2 is

$$\frac{\beta - \gamma}{\alpha - \gamma}.$$

Again from the foregoing values of β and γ, we have

$$2m(\beta - \gamma) = 2\frac{\theta}{\sqrt{3}} = 4\frac{m^2 e}{h^2},$$

to the order retained; and therefore, to this order,

$$k^2 = 4\frac{m^2}{h^2}e.$$

But $$K = \int_0^{\frac{1}{2}\pi} \frac{d\psi}{(1-k^2\sin^2\psi)^{\frac{1}{2}}}$$
$$= \int_0^{\frac{1}{2}\pi} (1+\tfrac{1}{2}k^2\sin^2\psi)\,d\psi$$

to the order of approximation: that is, to the order,

$$K = \tfrac{1}{2}\pi(1+\tfrac{1}{4}k^2)$$
$$= \tfrac{1}{2}\pi\left(1+\frac{m^2}{h^2}e\right).$$

Thus $$\Delta = 4\rho K - 2\pi$$
$$= 2\pi\left(1+3\frac{m^2}{h^2}-\frac{m^2e}{h^2}\right)\left(1+\frac{m^2}{h^2}e\right)-2\pi$$
$$= 2\pi\,.\,3\frac{m^2}{h^2};$$

and therefore there follows Prof. Einstein's inference from his theory that, to the order of approximation adopted, the perihelion of the moving body advances a fraction of a revolution equal to

$$3\frac{m^2}{h^2},$$

during each revolution.

6. As regards the approximation to u, we write

$$\phi-\varpi=\sigma, \qquad x=\frac{\pi\sigma}{2\rho K};$$

and as k^2 is small, the quantity q of the elliptic functions is

$$q=\frac{1}{16}k^2.$$

Now from the expression for $cn\,\frac{\sigma}{\rho}$, we have

$$cn\,\frac{\sigma}{\rho}=(1-4q\sin^2 x)\cos x,$$

so that we want $\cos x$. But

$$\frac{2\rho K}{\pi}=1+3\frac{m^2}{h^2},$$

and therefore

$$\cos x = \cos\left\{\left(1-3\frac{m^2}{h^2}\right)\sigma\right\}$$
$$= \cos\sigma + 3\frac{m^2}{h^2}\sigma\sin\sigma,$$

to the order retained, so that,

$$cn\,\frac{\sigma}{\rho} = \cos\sigma + 3\,\frac{m^2}{h^2}\,\sigma\sin\sigma - \frac{m^2}{h^2}\,e\sin^2\sigma\cos\sigma.$$

Again, from the expression for $dn\,\frac{\sigma}{\rho}$, we have

$$dn\,\frac{\sigma}{\rho} = 1-8q\sin^2 x$$

$$= 1-2\,\frac{m^2}{h^2}\,e\sin^2\sigma.$$

Consequently

$$\frac{1+cn\,\sigma/\rho}{1+dn\,\sigma/\rho} = \tfrac{1}{2}\,\frac{1+\cos\sigma+3m^2/h^2\,\sigma\sin\sigma - m^2/h^2\,e\sin^2\sigma\cos\sigma}{1-m^2/h^2\,e\sin^2\sigma}$$

$$= \tfrac{1}{2}\left(1+\cos\sigma+3\,\frac{m^2}{h^2}\,\sigma\sin\sigma+\frac{m^2}{h^2}\,e\sin^2\sigma\right)$$

to our order of approximation. Also

$$2m\gamma = 2\,\frac{m^2}{h^2} - 2\,\frac{m^2}{h^2}\,e,$$

so that $$\gamma = \frac{m}{h^2}(1-e);$$

and $$2m(\beta-\gamma) = 2\,\frac{\theta}{\sqrt{3}} = 4\,\frac{m^2 e}{h^2},$$

so that $$\beta-\gamma = 2\,\frac{m}{h^2}\,e.$$

Thus

$$u = \frac{m}{h^2}(1-e) + \frac{m}{h^2}\,e\left(1+\cos\sigma+3\,\frac{m^2}{h^2}\,\sigma\sin\sigma+\frac{m^2}{h^2}\,e\sin^2\sigma\right)$$

$$= \frac{m}{h^2}\left\{1+e\cos\sigma+3\,\frac{m^2 e}{h^2}\,\sigma\sin\sigma+\frac{m^2}{h^2}\,e^2\sin^2\sigma\right\}$$

$$= \frac{m}{h^2}\left\{1+e\cos(\phi-\varpi)+\frac{m^2}{h^2}\,e^2\sin^2(\phi-\varpi)\right.$$

$$\left. + 3\,\frac{m^2 e}{h^2}(\phi-\varpi)\sin(\phi-\varpi)\right\}.$$

7. If a closer approximation is desired for any body in which the quantity m^2/h^2 is not of so small an order as in the known solar system, fuller values of the roots α, β, γ of $\mathrm{U} = 0$ should be found, and can easily be found. But an inspection of the value of $\mathrm{G}^2+4\mathrm{H}^3$, upon which these roots depend, shows that, for any known bodies, the further approximations are ordinarily not worthy of account.

On the Refraction and Dispersion of Carbon Dioxide, Carbon Monoxide, and Methane.

By Clive Cuthbertson, O.B.E., F.R.S., and Maude Cuthbertson.

(Received January 2, 1920.)

In continuation of previous work* on the refraction and dispersion of gaseous elements and compounds within the limits of the visible spectrum, the refractivities of the gases named above were measured by the authors in 1914. Publication of results has been delayed by the war.

CARBON DIOXIDE.

The gas was prepared by heating a mixture of three parts of bichromate of potash and one part of sodium carbonate *in vacuo* and drying with phosphorus pentoxide. It was then condensed several times in liquid air and impurities pumped off. But, notwithstanding these precautions, tests by absorption in potassium hydroxide always indicated the presence of a small quantity (about 0·1 per cent.) of unabsorbed gas, which was assumed to be air and was allowed for in calculating the refractive index.

Refractive Index.

The refractive index was, as usual, determined for the green mercury line ($\lambda = 5461$) with a Jamin refractometer. Two trustworthy sets, each of four double experiments (*i.e.*, with pressure increasing and diminishing), gave the following results for CO_2 at 0° C. and 76 cm.:—$(\mu-1)\,10^7 = 4505$, 4500, 4508, 4504, 4500, 4507, 4507, 4509. The mean is 4505. The observations were made at the temperature of the room (about 17·5° C.) and between the pressures 30 and 50 cm. of mercury. The reduction for temperature was made by means of Chappuis's† coefficient $(1+{\cdot}00371t)$; that for pressure by Leduc's‡ formula—

$$P_0V_0/PV-1 = 102\times10^{-6}(P-P_0),$$

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* See C. and M. Cuthbertson, 'Roy. Soc. Proc.,' vol. 81, p. 440 (1908); vol. 83, pp. 149, 151, 171 (1909); vol. 84, p. 13 (1910); vol. 89, p. 361 (1913); 'Phil. Trans.,' A, vol. 213, p. 1 (1913). See also C. Cuthbertson, 'Phil. Trans.,' A, vol. 204, p. 323 (1905). C. Cuthbertson and E. B. R. Prideaux, 'Phil. Trans.,' A, vol. 205, p. 319 (1905). C. Cuthbertson and E. P. Metcalfe, 'Phil. Trans.,' A, vol. 207, p. 135 (1907); 'Roy. Soc. Proc.,' vol. 80, pp. 406, 411 (1908).

† P. Chappuis, 'Travaux et Mémoires de la Comité Internationale des Poids et Mesures,' vol. 13, p. 50 (1907).

‡ Leduc, 'Comptes Rendus,' vol. 123, p. 744.

In a previous paper,* however, it was pointed out that the practice of reducing refractivities to 0° C. and 76 cm. is not convenient for use in many theoretical investigations in the case of gases or vapours which do not conform closely to the laws of Boyle and Gay-Lussac. What is more often required is a standard which enables direct comparison to be made between the refractive effects of equal numbers of molecules of different gases; and, in such cases, we have usually reduced the refractivities to the values they would have had if the number of molecules per cubic centimetre had been equal to the number of molecules in a cubic centimetre of hydrogen at 0° C. and 76 cm. This value we denote by $(\mu-1)_{n.t.p.}\frac{D}{d_0 76}$. Taking the molecular weight of hydrogen as 2·0152, and that of carbon dioxide as 44·004, the theoretic weight of a litre of CO_2 is $0{\cdot}08985 \times \frac{44{\cdot}004}{2{\cdot}0152} = 1{\cdot}96195$ gr., Leduc's experimental density of CO_2 is 1·5288 (air = 1), and that of air 1·29316 gr. Hence the weight of a litre of CO_2 at 0° C. and 76 cm. is 1·977 gr. and

$$(\mu-1)_{n.t.p.}\frac{D}{d_0 76} = \frac{0{\cdot}0004505}{} \times \frac{1{\cdot}96195}{1{\cdot}977} = 0{\cdot}0004471.$$

Previous Work.

There have been numerous previous determinations of the refractivity of carbon dioxide, but few have attempted to attain an accuracy extending beyond the third significant figure. Among the more recent values which aim at a higher degree of exactitude are the following:—

Observer.	$(\mu-1)\,10^7$, $\lambda = 5461$.
Mascart	4554
Perreau	4515
G. W. Walker	4510 ± 5
Stuckert	4511
Grüschke	4512
Koch	4505

Our value agrees well with that of Koch. The discrepancies are, no doubt, largely due to the use of different coefficients of pressure and temperature in the reduction. Thus, had we used Walker's temperature coefficient $(1+0{\cdot}0038t)$, our result would have been 4512.

Dispersion of Carbon Dioxide.

The dispersion was measured in seven experiments, in nearly all of which 800 bands were counted. Table I shows the values obtained.

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* 'Phil. Trans.,' A, vol. 213 (1913).

Table I.—Dispersion of Carbon Dioxide.

$\lambda\times10^8$.	$(\mu-1)\,10^8$.		Difference.	$(\mu-1)_{n.t.p.}10^8\frac{D}{d_0 76}$.	Calculated.
	Observed.	Calculated.			
6708	44,714	44,718	+4	44,377	44,381
6438	44,771	44,773	+2	44,434	
5790	44,940	44,938	−2	44,601	
5770	44,947	44,944	−3	44,608	
5461	45,050	45,049	−1	44,710	
5209	45,148	45,147	−1	44,806	
5085	45,201	45,199	−2	44,858	
4800	45,342	45,341	−1	44,999	44,998

Column 3 gives the values calculated from the formula

$$(\mu-1)_{n.t.p.} = \frac{6\cdot2144\times10^{27}}{(14097)\,10^{27}-n^2}.$$

Column 5 gives the observed values, reduced to the standard

$$(\mu-1)_{n.t.p.}\,\frac{D}{d_0 76}.$$

Previous Work on Dispersion.

The dispersion of carbon dioxide has been measured, in recent years, by Mascart, Perreau, Rentschler, Koch, Stuckert, and Grüschke, and at high pressures by Siertzema and Haas. The degree of accuracy attained by these observers is best tested by plotting n_0^2, the square of the free frequency of the electron (assuming only one kind to exist) against $1/\mu-1$ for different frequencies. The points should fall on a straight line. Tried in this way, the values of Perreau and Siertzema and Haas give the most regular results, and we are happy to find that our values for the dispersive power are in almost exact agreement with theirs. Thus the three determinations lead to the following values for λ_0, the wave-length corresponding to n_0:—

Siertzema and Haas	$\lambda_0 = 798\times10^{-8}$
C. and M. Cuthbertson	$= 799\times10^{-8}$
Perreau	$= 800\times10^{-8}$

Carbon Monoxide.

The gas was prepared by the action of formic acid on concentrated sulphuric acid *in vacuo*, and, after passing over dry potash and phosphorus pentoxide, was condensed in liquid air boiling under reduced pressure. The liquid carbon monoxide was then allowed to warm till all uncondensable impurities had been swept out of the apparatus, and the fraction remaining was boiled off and stored. On testing by explosion with oxygen no impurities were found.

Refractive Index.

Four double experiments gave, for the green mercury line,

$$(\mu-1)\,10^7 = 3362,\ 3365,\ 3364,\ 3364. \quad \text{Mean } 3364.$$

These experiments were reduced by the formula

$$\nu-1 = (\mu-1)\,\frac{76}{\mathrm{P}}\,\frac{\mathrm{T}}{273}.$$

Previous Work.

The refractivity has been measured frequently, with the following results at λ = 5461.

Observer.	$(\mu-1)\,10^7$.
Mascart	3356
Perreau	3365
Koch	3361
Grüschke	3361

Our value agrees well with that of the last three experiments.

Dispersion.

The dispersion was measured in ten experiments, in each of which nearly 600 bands were counted. Table II gives the results :—

Table II.—Dispersion of Carbon Monoxide.

$\lambda \times 10^8$.	$(\mu-1)\,10^8$.		Difference.
	Observed.	Calculated.	
6708	33,327	33,326	−1
6438	33,379	33,379	0
5790	33,535	33,536	+1
5770	33,542	33,542	0
5461	33,640	33,640	0
5209	33,732	33,733	+1
5085	33,782	33,784	+2
4800	33,920	33,918	−2

The values given in column 3 were calculated from

$$\mu-1 = \frac{3{\cdot}64067 \times 10^{27}}{11{,}124 \times 10^{27} - n^2}.$$

Previous Work on Dispersion.

The dispersion was measured by all those named above, with remarkably concordant results. The values of λ_0 deduced from their figures compare as follows with those derived from our results:—

	$\lambda_0 \times 10^8$.
Mascart	901
Perreau	890
Koch	901
Grüschke	880
Cuthbertson	899

METHANE.

Previous experimenters have had difficulty in obtaining this gas pure. Through the kindness of Messrs. Colin Campbell and Parker, of Manchester University, we were supplied with samples purified from hydrogen by the new method which they have devised.*

Refractive Index of Methane.

Five double experiments with this gas gave for the green mercury line: $(\mu-1)\,10^7 = 4417, 4412, 4414, 4416{\cdot}5, 4414{\cdot}5$. Mean 4415.

Previous Work.

Among recent determinations of the refractivity of methane are:—

	$(\mu-1)\,10^7$.
St. Loria†	4468
Kessler‡	4435
Koch§	4407

These values are not concordant, probably owing to the difficulty of purifying the gas.

Dispersion of Methane.

The dispersion was measured in eight experiments, in three of which 800 bands were counted, and in the rest, 500 bands. The results are shown in the following Table:—

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* C. Campbell and A. Parker, 'Trans. Chem. Soc.,' vol. 103, p. 1292 (1913).

† S. Loria, 'Ann. d. Physik,' vol. 29, p. 605 (1909).

‡ Kessler, 'Diss. Halle,' 1909 (Quoted by Loria in 'Lichtbrechung in Gasen als physikalisches und chemisches Problem').

§ J. Koch, 'Arkiv for Mat. Astr. och Fysik,' vol. 9 (6), 1913.

Table III.—Dispersion of Methane.

$\lambda \times 10^8$.	$(\mu-1)\,10^8$.		Difference.
	Observed.	Calculated.	
6708	43,759	43,760	+1
6438	43,824	43,824	0
5790	44,021	44,021	0
5770	44,029	44,028	−1
5461	44,150	44,150	0
5209	44,267	44,266	−1
5085	44,330	44,330	0
4800	44,497	44,498	+1

The numbers in the third column are calculated from the formula

$$\mu-1=\frac{5\cdot02763\times10^{27}}{11689\cdot3\times10^{27}-n^2}.$$

Previous Work on Dispersion.

The same observers measured the dispersion of methane. Their results are fairly concordant, and we find the slope of our dispersion curve practically identical with that of Koch. The values of λ_0 deduced from the figures of others compare, as follows, with our own :—

	$\lambda_0 \times 10^8$
St. Loria	1072
Kessler	948
Koch	883
Cuthbertson	877

Remarks.

The work described above was undertaken with the object of arriving at an estimate of the refractive power of the carbon atom by comparing the refraction and dispersion of oxygen and hydrogen with those of the simplest carbon compounds containing atoms of these gases. On the assumption that refractivity is an atomic property which is nearly constant, notwithstanding chemical change, the values of $(\mu-1)_C$, derived from CO_2 and CH_4, should be concordant, while that derived from CO should show an instructive variation, due to the unsaturation of the carbon atom. Moreover, the concordance should be exhibited not only in the refractivity, but in the numerators and denominators of the expression

$$\mu-1=\frac{C}{n_0^2-n^2}$$

which respectively represent the number of dispersion electrons present (C) and the square of their free frequency (n_0^2).

In a previous paper* we have shown that the refraction and dispersion of hydrogen, oxygen, and nitrogen can be expressed as follows:—

Gas.	$\mu-1$.
Hydrogen	$\dfrac{1{\cdot}692\times10^{27}}{12{,}409\times10^{27}-n^2}$
Oxygen	$\dfrac{3{\cdot}397\times10^{27}}{12{,}804\times10^{27}-n^2}$
Nitrogen	$\dfrac{5{\cdot}0345\times10^{27}}{17{,}095\times10^{27}-n^2}$

The numerators of these expressions which, on Drude's theory, should be proportional to the number of "dispersion" or "valency" electrons, are almost exactly in the ratio of 1, 2, 3; and the free frequencies increase with the valency, though not in the same proportion. It was, therefore, to be hoped that the corresponding expression for one *atom* of quadrivalent carbon would have, as numerator, approximately $1{\cdot}692\times4\times10^{27}/2 = 3{\cdot}384\times10^{27}$, and as denominator a squared free frequency higher than $17{,}095\times10^{27}$.

This expectation has not been fulfilled. Calculating the formula for the refraction and dispersion of carbon as shown below for the case of carbon dioxide,† we obtain the following three expressions:—

		$\mu_\infty-1$.
From carbon dioxide	$\mu-1 = \dfrac{2{\cdot}8837\times10^{27}}{16{,}745\times10^{27}-n^2}$	$= 0{\cdot}00017221$,
From carbon monoxide ...	$\mu-1 = \dfrac{1{\cdot}9876\times10^{27}}{10{,}213\times10^{27}-n^2}$	$= 0{\cdot}00019461$,
From methane	$\mu-1 = \dfrac{1{\cdot}6720\times10^{27}}{10{,}623\times10^{27}-n^2}$	$= 0{\cdot}00015740$.

It is evident that the "additive law" breaks down completely. Not only do the refractivities for λ_∞ vary widely, but the figures corresponding to

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* 'Roy. Soc. Proc.,' vol. 83, p. 151 (1909).

	$\lambda = 6708\times10^{-8}$	$\lambda = 4800\times10^{-8}$
† For carbon dioxide $(\mu-1)_{n.t.p.}\,10^8\,\dfrac{D}{d_0 76}$ (See Table I, column 6)	$=$ 44,381	44,998
Deduct the corresponding values for O_2	26,952	27,366
Estimated refractivity of C	17,429	17,632

From these two values we obtain

$$\mu-1 = \frac{2{\cdot}8837\times10^{27}}{16{,}745\times10^{27}-n^2}.$$

the relative numbers of electrons and the free frequencies are hopelessly discordant.

The inference must be that the forces which control the motion of a "dispersion electron" in an atom are profoundly affected by the proximity of another atom in combination with it. If the two atoms are of the same sort, as in the molecule of an elementary gas, a similar change, perhaps large in amount, must also occur; but it is probably simpler in character, owing to the fact that the free frequencies in both atoms are originally the same and are altered to the same extent. On this hypothesis, at any rate, we might explain why the integral relation (1, 2, 3) between the formulæ for the refractivities of hydrogen, oxygen, and nitrogen can subsist in spite of the changes which must have resulted in each atom on the formation of the diatomic molecule.

The present paper forms probably the last chapter of a research, begun in 1902, on the refractivity of gaseous elements and compounds. The results are to be found in the papers quoted (p. 152) above, and in two papers by one of us, published in the 'Philosophical Magazine.'* We think that a sufficient body of accurate measurements now exists to provide material for testing any theory of atomic structure which may be put forward to account for the optical phenomena.

We have great pleasure in expressing our indebtedness to the Royal Society for the allotment of a grant in aid of the above work, and to Messrs. Campbell and Parker for the gift of pure specimens of methane.

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* 'Phil. Mag.,' p. 69 (January, 1911); p. 592 (April, 1913).

The Capacity Coefficients of Spherical Conductors.

By ALEXANDER RUSSELL, M.A., D.Sc., M.I.E.E.

(Communicated by Dr. C. Chree, F.R.S. Received January 5, 1920.)

Maxwell* pointed out that the self-capacity coefficient of a conductor is numerically equal to its charge when its potential is unity and all neighbouring conductors are at zero potential. He considered that the "proper definition of the capacity of a conductor" is to define it as being equal to the self-capacity coefficient. Adopting this definition, we may consider that the self-capacity coefficient is the capacity of the condenser formed by the conductor, on the one side, and, on the other side, all neighbouring conductors connected with the earth. This gives a simple physical meaning to the self-capacity coefficient, and in one or two simple cases it enables us to compute its value. In the case of a spherical conductor, however, we can give an equally simple way of regarding it, which leads to easier methods of computing its value. As a knowledge of the self-capacity coefficients of spheres is essential in certain practical problems, for instance, when computing the electric stress at which a spark will occur between unequal spherical electrodes when the dielectric between them is at a given temperature and pressure, simplified methods of finding their values are useful. It is proved below that the self-capacity coefficient of a spherical conductor equals its radius together with the capacity of the condenser formed between the surface of the sphere and the images in the sphere of all external conductors, including the earth connected in parallel.

Many of the formulæ given by the author in his papers† are connected by very simple relations. For brevity, we shall refer to these papers as X and Y respectively. The approximate formulæ given in Y for spherical condensers can be usefully employed for computing the capacity coefficients for external spheres, and, conversely, we can use the tables given by Kelvin‡ and in X, p. 529, for computing the values of the capacities of spherical condensers.

The relations show that in many cases the values of the coefficients and the capacities can be written down almost at once without even using logarithmic tables. We shall also show that the theorem can be applied to simplifying the problem of finding the capacity between a sphere and large distant conductors or of finding the capacity between a small sphere placed in a large cavity of given shape in a conductor.

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* 'Electricity and Magnetism,' vol. 1, § 87.

† 'Roy. Soc. Proc.,' vol. 82, p. 524; vol. 94, p. 206.

‡ Kelvin, Reprint, p. 96.

General Theorem.

If a conducting sphere A (fig. 1) be in the presence of a conductor B, and

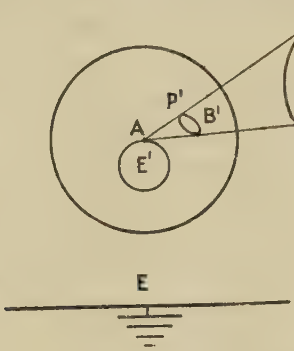

FIG. 1.—AP′. AP = a^2. B′ and E′ are the images of B and the Earth.

if the earth E be at a considerable distance away from the sphere, then the self-capacity coefficient k_{11} of A is given by

$$k_{11} = a + C, \tag{1}$$

where a is the radius of the sphere A, and C is the capacity between the image B′ of B in the sphere and the surface of the sphere.

To prove this, let E be the earth, supposed an infinite plane, and let B and E be joined in parallel. The potential of B will be zero. Let a charge q_1 be given to A. There will be induced charges on B and E. Let B′ and E′ be the inverse surfaces of B and E with regard to the sphere. Then, by the theory of inversion*, a certain charge q' on B′ and E′ will, when B and E are removed, produce with q_1 the same potential v_1 at the surface of the sphere A as the actual distribution does. If C be the capacity between B′ and E′ in parallel and the surface of the sphere A, we have

$$q' = C(o - v_1).$$

The quantity of electricity on the inside of the surface of A will be $-q'$. Therefore there will be a charge $q_1 + q'$ on the outer surface, and since B and E are removed, we have the sphere A in infinite space, and so

$$q_1 + q' = av_1,$$

for the capacity of the sphere is a.

Hence $$q_1 = (a + C)v_1.$$

But since v_2 is zero we have $q_1 = k_{11}v_1$, and hence

$$k_{11} = a + C. \tag{1A}$$

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* J. J. Thomson, 'Electricity and Magnetism,' 4th ed., p. 180.

If the earth E be at a considerable distance away, the sphere E′ will be very minute. Its capacity will, therefore, be negligibly small. Hence, in this case, C is simply the capacity between B′ and A, which proves the theorem. It is obvious that this theorem applies when there are any number of conductors like B in the neighbourhood of the sphere. The condenser C is formed on the one side by all their images connected in parallel, and on the other, by the surface of the sphere. We see at once that the self-capacity coefficient of a sphere is always greater than its radius, and that it is very large when any of the conductors are close to it.

When B forms a continuous conductor entirely enclosing A, we know (Y, p. 208) that the capacity between A and B $= k_{11} = -k_{12}$. Thus, if C_1 be the capacity between a sphere and a conductor entirely surrounding it, and C_2 be the capacity between the surface of the sphere and the image (or inverse) of the surrounding surface in the sphere, we always have

$$C_1 = a + C_2. \qquad (2)$$

The Capacity Coefficients of Spheres.

In the following investigation it is found convenient to denote the capacity coefficients k_{11}, k_{22}, and k_{12} of a system of two spheres by $f_{11}(a, b, c)$, $f_{22}(a, b, c)$, and $f_{12}(a, b, c)$ respectively, where a and b are the radii of the spheres and c is the distance between their centres, c being greater than $a+b$. We shall also denote the capacity of a condenser formed by an outer sphere of radius a_1, and an inner sphere of radius b_1 by $F(a_1, b_1, c_1)$, where c_1 is the distance between their centres. It is to be noticed that a_1 must be greater than b_1+c_1, but b_1 can be greater or less than c_1. We also have $F(a_1, b_1, 0) = a_1b_1/(a_1-b_1)$.

Kelvin's* and Maxwell's† formulæ for the self-capacity coefficients of a system of two spheres can be readily proved by (1) and (2). We shall give the proof in full as the steps give relations useful in computation. In order to bring out clearly the relations between the various systems of condensers considered in this theorem, we shall use the functions (α, β, ω) and $(\alpha_1, \beta_1, \omega_1)$ used in X and Y. Their definitions are as follows:—

External Spheres.

$$\left.\begin{aligned} \cosh\alpha &= \frac{c^2+a^2-b^2}{2ca} \\ \cosh\beta &= \frac{c^2+b^2-a^2}{2bc} \\ \cosh\omega &= \frac{c^2-a^2-b^2}{2ab} \end{aligned}\right\}, \qquad (\mathrm{I})$$

Internal Spheres.

$$\left.\begin{aligned} \cosh\alpha_1 &= \frac{a_1^2+c_1^2-b_1^2}{2c_1a_1} \\ \cosh\beta_1 &= \frac{a_1^2-b_1^2-c_1^2}{2b_1c_1} \\ \cosh\omega_1 &= \frac{a_1^2+b_1^2-c_1^2}{2a_1b_1} \end{aligned}\right\}. \qquad (\mathrm{II})$$

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* Kelvin, Reprint, p. 93.

† 'Electricity and Magnetism,' vol. 1, § 173.

We also have,

External Spheres.

$$\left.\begin{aligned} \omega &= \alpha+\beta \\ \sinh\alpha = \frac{r}{a},\quad &\sinh\beta = \frac{r}{b} \\ \sinh\omega &= \frac{cr}{ab} \end{aligned}\right\}, \quad \text{(III)}$$

We also have,

Internal Spheres.

$$\left.\begin{aligned} \omega_1 &= \beta_1-\alpha_1 \\ \sinh\alpha_1 = \frac{r_1}{a_1},\quad &\sinh\beta_1 = \frac{r_1}{b_1} \\ \text{and}\quad \sinh\omega_1 &= \frac{c_1 r_1}{a_1 b_1} \end{aligned}\right\}, \quad \text{(IV)}$$

where r and r_1 are the radii of the orthogonal spheres.

Let us consider two spheres of radii a and b respectively (fig. 2). Let B_1 be the image of B in the sphere A. Then by (1)

$$f_{11}(a, b, c) = a+F(a_1, b_1, c_1), \tag{3}$$

where*

$$a_1 = a, \qquad b_1 = \frac{a^2}{c^2-b^2}\,b, \qquad \text{and} \qquad c_1 = \frac{a^2}{c^2-b^2}\,c. \tag{V}$$

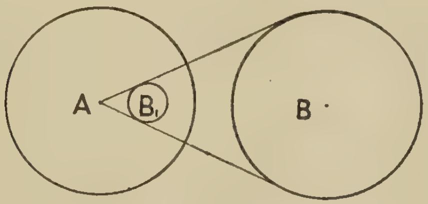

FIG. 2.

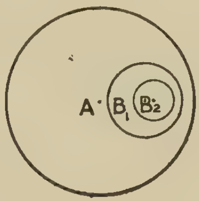

FIG. 3.

FIG. 2.—$k_{11} = a+$the capacity between A and B_1.

FIG. 3.—The capacity between A and B_1 = the radius of B_1 plus the capacity between B_1 and B_2.

Let us now invert the sphere A with respect to the sphere B_1, and let the image be B_2 (fig. 3), we get by (2)

$$F(a_1, b_1, c_1) = b_1+F(a_2, b_2, c_2), \tag{4}$$

where

$$a_2 = b_1, \qquad b_2 = \frac{{b_1}^2}{{a_1}^2-{c_1}^2}\,a_1, \qquad \text{and} \qquad c_2 = \frac{{b_1}^2}{{a_1}^2-{c_1}^2}\,c_1. \tag{VI}$$

We then invert B_1 with respect to B_2 and so on. Thus, by adding up the equations (3), (4) ... we get

$$f_{11}(a, b, c) = a+b_1+b_2+\ldots, \tag{5}$$

and by adding up the same equations, beginning with (4) we get

$$F(a_1, b_1, c_1) = b_1+b_2+b_3+\ldots. \tag{6}$$

Substituting in (II) for a_1, b_1 and c_1, their values from (V), we get

$$\cosh\omega_1 = \frac{{a_1}^2+{b_1}^2-{c_1}^2}{2a_1b_1} = \frac{a^2+a^4b^2/(c^2-b^2)^2-a^4c^2/(c^2-b^2)^2}{2a^3b/(c^2-b^2)}$$

$$= \frac{c^2-a^2-b^2}{2ab} = \cosh\omega.$$

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* J. J. Thomson, *ibid.*, p. 177.

Hence $\omega_1 = \omega$. Similarly $\alpha_1 = \alpha$, and thus since $\beta_1 = \omega_1 + \alpha_1$, we get $\beta_1 = \alpha + \omega$. We also have $\sinh \alpha = r/a = \sinh \alpha_1 = r_1/a_1$, and thus $r = r_1$. In the same way we find that $\omega_2 = \omega_1$, $\alpha_2 = \beta_1$, and therefore,

$$\beta_2 = \alpha_2 + \omega_2 = \alpha + 2\omega.$$

Hence also $r_1 = r_2$, etc.

Therefore $$b_n = \frac{r_n}{\sinh \beta_n} = \frac{r}{\sinh(\alpha + n\omega)}.$$

Hence substituting in (5) and (6) we get

$$f_{11}(a, b, c) = \sum_0^\infty \frac{r}{\sinh(\alpha + n\omega)}, \qquad (7)$$

and $$F(a_1, b_1, c_1) = \sum_1^\infty \frac{r_1}{\sinh(\alpha_1 + n\omega_1)}$$

$$= \sum_0^\infty \frac{r_1}{\sinh(\beta_1 + n\omega_1)}. \qquad (8)$$

Formula (7) is Maxwell's modification of Kelvin's formula,* and (8) agrees with (4) and (5) of Y.

Since we have

$$f_{11}(ma, mb, mc) = m f_{11}(a, b, c), \qquad (9)$$

and $$F(ma, mb, mc) = m F(a, b, c), \qquad (10)$$

the equations (3) and (4) may be written in the form

$$f_{11}(a, b, c) = a + \frac{a^2}{c^2 - b^2} F\left(\frac{c^2 - b^2}{a}, b, c\right), \qquad (11)$$

$$= a + \frac{a^2}{c^2 - b^2} F(a_1, b_1, c_1).$$

Note that a_1, b_1, and c_1 in this formula differ from the a_1, b_1, and c_1 in formula (3).

We have also, $$F(a_1, b_1, c_1) = b_1 + \frac{b_1^2}{a_1^2 - c_1^2} F\left(\frac{a_1^2 - c_1^2}{b_1}, a_1, c_1\right) \qquad (12)$$

$$= b_1 + \frac{b_1^2}{a_1^2 - c_1^2} F(a_2, b_2, c_2).$$

In general we can write, when n is greater than unity

$$F(a_{n-1}, b_{n-1}, c_{n-1}) = \frac{r \sinh(\alpha + \overline{n-2}\,\omega)}{\sinh \alpha \sinh \beta} + \frac{\sinh(\alpha + \overline{n-2}\,\omega)}{\sinh(\alpha + n\omega)} F(a_n, b_n, c_n), \qquad (13)$$

where $$a_n = \frac{r \sinh(\alpha + n\omega)}{\sinh \alpha \sinh \beta}; \qquad b_n = \frac{r \sinh(\alpha + \overline{n-1}\,\omega)}{\sinh \alpha \sinh \beta};$$

and $$c_n = c = \frac{r \sinh \omega}{\sinh \alpha \sinh \beta}. \qquad \text{(VII)}$$

* Kelvin, Reprint, p. 93.

From formula (28) given below, it will be seen that when $c_n^2/(a_n-b_n)^2$ can be neglected compared with unity, we can write

$$F(a_n, b_n, c_n) = a_n b_n/(a_n-b_n), \tag{14}$$

which is the formula for a concentric spherical condenser. From (VII) also we have

$$\frac{c_n}{a_n-b_n} = \frac{\cosh(\omega/2)}{\cosh\{\alpha+(2n-1)\omega/2\}}$$

Hence, except when ω is very small, in which case the spheres are very close together and the other simpler formulæ given in X and Y become applicable, we do not need to go to a high value of n before we can use (14).

The equations (11) and (12) can also be written in the inverse form

$$F(a_1, b_1, c_1) = \frac{a_1^2}{c_1^2-b_1^2} f_{11}\left(\frac{c_1^2-b_1^2}{a_1}, b_1, c_1\right) - a_1 \tag{15}$$

and

$$F(a_1, b_1, c_1) = \frac{a_1^2}{b_1^2-c_1^2} F\left(b_1, \frac{b_1^2-c_1^2}{a_1}, c_1\right) - a_1. \tag{16}$$

The Mutual Coefficient.

It is more difficult to prove by this method Kelvin's formula for the mutual coefficient which Maxwell gives in the form

$$f_{12}(a, b, c) = \sum_1^\infty \frac{r}{\sinh n\omega}. \tag{17}$$

It is easy, however, to express its value in terms of the capacity of a spherical condenser. We see from (17) that the mutual coefficient has a constant value for all the families of spheres which have the same r and ω. Let us consider the member of the family for which the radius b of B is infinite (fig. 4). In this case $\beta = 0$, and therefore the radius a_0 of the sphere A_0 in fig. 4 is given by

$$a_0 = r/\sinh \omega.$$

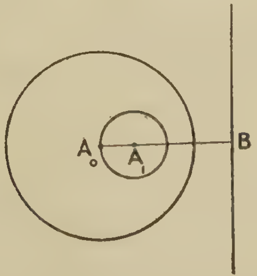

FIG. 4.—$-k_{12}$ equals the radius of A_0 plus the capacity between A_0 and A_1.

We see by the formula for $\cosh \omega_1$ given in (II) that the distance $c-b$ of the centre of the sphere A from the plane is $a_0 \cosh \omega$, that is, $r \coth \omega$.

As a system consisting of a plane and a sphere is the limiting case of a spherical condenser when the outer radius becomes infinite, we have by Y (p. 207), $k_{11} = -k_{12}$, and thus by (1),

$$-k_{12} = a_0 + \mathrm{F}(a_0, r_1, r_1)$$

where r_1 is the radius of the image of the plane in the sphere. Since $r_1 = a_0^2/(2r\coth\omega) = r/\sinh 2\omega$, we have

$$-k_{12} = \frac{r}{\sinh\omega} + \mathrm{F}\left(\frac{r}{\sinh\omega}, \frac{r}{\sinh 2\omega}, \frac{r}{\sinh 2\omega}\right), \tag{18}$$

or

$$-\frac{c}{ab} f_{12}(a, b, c) = 1 + \frac{ab}{c^2-a^2-b^2}\mathrm{F}\left(\frac{c^2-a^2-b^2}{ab}, 1, 1\right). \tag{19}$$

We can also show that

$$f_{12}(a, b, c) = (c_1/c) f_{12}(ax, b/x, c_1), \tag{20}$$

where $c_1^2 = c^2-(a+b)^2+(ax+b/x)^2$, and x is any number.

This follows from (17), because from (I), $\omega_1 = \omega$, and therefore, $\sinh\omega_1 = \sinh\omega$, and so $c_1 r_1 = cr$.

Thus $(c_1/c) r_1/\sinh n\omega_1 = r/\sinh n\omega$ and hence (20) follows from (17).

If we put $x = (b/a)^{\frac{1}{2}}$, (20) becomes

$$f_{12}(a, b, c) = (c_1/c) f_{12}(a_1, a_1, c_1), \tag{21}$$

where $a_1^2 = ab$, and $c_1^2 = c^2-(a-b)^2$.

We also have

$$f_{12}(a, b, c) = f_{12}(a_2, a_2, c_2), \tag{22}$$

where $a_2^2 = ab\{1-(a-b)^2/c^2\}$ and $c_2 = c-(a-b)^2/c$.

This follows at once from (21). Hence the mutual coefficient between any two spheres can be found from the Tables* for the mutual coefficients of equal spheres.

Miscellaneous Relations between the Coefficients and Capacities.

If we define the capacity C_0 between two conductors as the ratio of the charge on one of them to the difference of potential between them when they are given equal and opposite charges, we have by X, p. 258,

$$C_0 = \frac{k_{11}k_{22}-k_{12}^2}{k_{11}+k_{22}+2k_{12}}. \tag{23}$$

It readily follows that $k_{11}-C_0$, $k_{22}-C_0$ and $C_0-k_{11}k_{22}/(k_{11}+k_{22})$ are all positive. Hence C_0 lies in value between the smaller of the self-capacity coefficients and $k_{11}k_{22}/(k_{11}+k_{22})$. We may also write (23) in the form

$$-k_{12} = C_0 - \{(k_{11}-C_0)(k_{22}-C_0)\}^{\frac{1}{2}}, \tag{24}$$

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* Kelvin, Reprint, p. 96; A. Russell, 'Roy. Soc. Proc.,' vol. 82, p. 529; 'Journ. of the Inst. of Elec. Engin.,' vol. 48, p. 257.

the minus sign being written before the square root as $-k_{12}$ is always less than C_0.

It is easy to show by (7), (8), and (17) that if C_0 be the capacity between the spheres of the system $(b, b, b^2/a)$, then

$$2C_0 = f_{11}(b, b, b^2/a) - f_{12}(b, b, b^2/a) = b + F(b, a, a) \tag{25}$$

Similarly we can show that

$$2C_0 = f_{11}(1, 1, c) - f_{12}(1, 1, c) = -\sqrt{c+2}\, f_{12}(1, 1, \sqrt{c+2}) \tag{26}$$

or

$$2f_0(1, 1, c) = -\sqrt{c+2}\, f_{12}(1, 1, \sqrt{c+2}),$$

and by (19)

$$f_0(1, 1, c) = \tfrac{1}{2} + \frac{1}{2c} F(c, 1, 1), \tag{27}$$

where $f_0(1, 1, c)$ denotes the capacity C_0 between the spheres, 1, 1, of the system $(1, 1, c)$.

The following examples illustrate the practical use of the theorems given above :—

Numerical Examples.

1. A system of two spheres, each 1 cm. in radius and 2 cm. apart.

In this case by (11),

$$k_{11} = f_{11}(1, 1, 4) = 1 + \frac{1}{15} F(15, 1, 4),$$

and by (12)

$$F(15, 1, 4) = 1 + \frac{1}{209} F(209, 15, 4).$$

Keeping the first two terms only in the expansion given in Y, (21) of $F(a, b, c)$ in ascending powers of $c^2/(b-a)^2$, we have

$$F(a, b, c) = \frac{ab}{a-b}\left\{1 + \frac{1}{a/b + b/a + 1}\,\frac{c^2}{(a-b)^2} + \ldots\right\}. \tag{28}$$

Hence

$$F(209, 15, 4) = \frac{209 \times 15}{194}(1 + 0\cdot0000284).$$

Therefore

$$k_{11} = 1 + \frac{1}{15} + \frac{1}{194}(1\cdot0000284) = 1\cdot071\ \ 821\ \ 4.$$

The value given by Kelvin* is 1·071 82.

If we had assumed that F (209, 15, 4) could be calculated by the ordinary formula for a concentric spherical condenser, namely, $209 \times 15/(209-15)$, the error introduced by this assumption when determining k_{11} would only be unity in the seventh decimal place.

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* Kelvin, Reprint, p. 96.

Similarly by (19) we have

$$-4k_{12} = -4f_{12}(1, 1, 4) = 1 + F(14, 1, 1),$$

and by (12),
$$F(14, 1, 1) = 1 + \frac{1}{195} F(195, 14, 1)$$

and hence by (28)
$$= 1 + \frac{14}{181}(1{\cdot}0000020).$$

Therefore
$$-k_{12} = 0{\cdot}269 \quad 238 \quad 4.$$

Kelvin (*loc. cit. ante*) gives the value 0·269 24.

By (27) we also have

$$f_0(1, 1, 4) = \frac{1}{2} + \frac{1}{8} F(4, 1, 1),$$

and by (12),
$$F(4, 1, 1) = 1 + \frac{1}{15} F(15, 4, 1),$$

$$F(15, 4, 1) = 4 + \frac{1}{14} F(56, 15, 1),$$

and
$$F(56, 15, 1) = 15 + \frac{15}{209} F(209, 56, 1)$$

$$= 15 + \frac{15 \times 56}{153} \text{ very approximately.}$$

Hence
$$C_0 = f_0(1, 1, 4) = \frac{1}{2} + \frac{1}{8} + \frac{1}{30} + \frac{1}{112} + \frac{1}{306}$$

$$= 0{\cdot}670 \quad 529 \quad 88.$$

Using the values found above, we have

$$C_0 = \tfrac{1}{2}(k_{11} - k_{12}) = 0{\cdot}670 \quad 529 \quad 9.$$

2. If we consider the spherical condenser the capacity of which is F (8, 1, 3) and use the inverse formula (15), we get

$$F(8, 1, 3) = 8f_{11}(1, 1, 3) - 8.$$

From Kelvin's Table, $f_{11}(1, 1, 3) = 1{\cdot}146 \quad 29$, and thus

$$F(8, 1, 3) = 1{\cdot}170 \quad 32.$$

To check this value, we get by (12)

$$F(8, 1, 3) = 1 + \frac{1}{55} F(55, 8, 3),$$

and also,
$$F(55, 8, 3) = 8 + \frac{8}{377} F(377, 55, 3).$$

Hence
$$F(8, 1, 3) = 1 + \frac{8}{55} + \frac{8}{322}(1{\cdot}000 \quad 001 \quad 4)$$

$$= 1{\cdot}170 \quad 299 \quad 3.$$

Hence also
$$f_{11}(1, 1, 3) = 1{\cdot}146 \quad 287 \quad 7.$$

Spheres close together.

When the external spheres are at a distance x apart which is small compared with either radius, the coefficients can be easily computed by the help of Y (16), which gives the capacity of a spherical condenser when the spheres are close together.

As an example of the use of this formula let us find the capacity C between a sphere of radius a which is at a very small distance x from an infinite plane. Making the radius of the outer sphere infinite in Y, (16) and neglecting terms containing squares and higher powers of x/a, we get

$$C = k_{11} = -k_{12} = a\left(1+\frac{x}{3a}\right)\left(\gamma+\tfrac{1}{2}\log\frac{2a}{x}+\frac{x}{9a}\right), \qquad (29)$$

where $\gamma =$ Euler's constant $= 0{\cdot}577216$.

Now the capacity C equals a plus the capacity between the sphere and the image of the plane in the sphere. Thus

$$C = a+F\left(a,\ \frac{a^2}{2(a+x)},\ \frac{a^2}{2(a+x)}\right). \qquad (30)$$

This equation is exact.

Hence also $\qquad F(a, c, c)+a, \qquad (31)$

is the capacity between a sphere of a radius a and a plane at a distance x, which equals $a^2/(2c)-a$, from it. For example, when $a = 201$ and $c = 100$, we get $x = 1{\cdot}005$, and thus by (29)

$$F(201, 100, 100)+201 = 201\left(1+\frac{1}{600}\right)\left(0{\cdot}577\ 216+\log 20+\frac{1}{1800}\right)$$

$$= 719{\cdot}47,$$

and thus $F(201, 100, 100) = 518{\cdot}47$.

This is correct to the last figure (see Y, p. 214).

The computation of the capacity C between a sphere and a plane is very simple when the distance between them is large compared with the radius of the sphere. For instance, when the radius of the sphere is 10 cm., and the height of its centre above the plane is 100 cm., we get by (30)

$$C = 10+F(10, \tfrac{1}{2}, \tfrac{1}{2})$$

$$= 10+\frac{10\times\frac{1}{2}}{10-\frac{1}{2}} \text{ approx.}$$

$$= 10{\cdot}526\ \ 32.$$

The true value is $10{\cdot}526\ \ 39$.

Approximate Formulæ for the Capacity between a Sphere and a Large Conductor.

If k_{11} be the self-capacity of the sphere, and k_{22} be the self-capacity of all the neighbouring conductors connected in parallel, we have shown above that the capacity C_0 between the sphere and the conductors lies in value between k_{11} and $k_{11} \times k_{22}/(k_{22}+k_{11})$. Hence when k_{22} is large, C_0 is practically equal to k_{11} and thus by (1)

$$C_0 = a + C_1, \tag{32}$$

where C_1 is the capacity between the surface of the sphere and all the images of the conductors in the sphere connected in parallel. If the conductors are distant from the sphere their images will be small and close to the centre of the sphere. In this case C_1 will be very slightly greater than the capacity C' of the images if they were in infinite space. We therefore have

$$C_0 = a + C', \tag{33}$$

approximately. Hence when the capacity C' of the image is known, we can find an approximate value of C_0 at once.

1. Consider a small sphere of radius a placed between two parallel and infinite conducting planes at distances b and c from its centre, where a/b and a/c can be neglected compared with unity. The images of the two planes will obviously be two spheres of radii $a^2/(2b)$ and $a^2/(2c)$ touching one another at the centre of A (fig. 5). The capacity* C' of the images is given by

$$C' = -\frac{a^2}{2(b+c)}\left\{\psi\left(\frac{b}{b+c}\right)+\psi\left(\frac{c}{b+c}\right)+2\gamma\right\}, \tag{34}$$

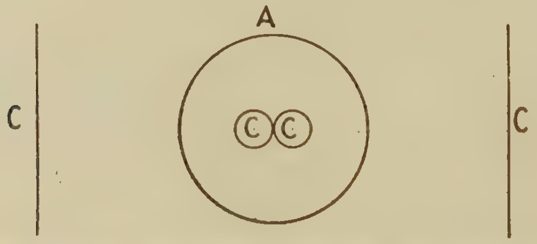

Fig. 5.—The capacity between the sphere A and the two infinite planes equals the radius of the sphere A plus the capacity of the condenser formed by A and the two image spheres touching at its centre.

where $\psi(x)$ is the logarithmic derivate of the gamma function. If we write

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* A. Russell, 'Alternating Currents,' vol. 1, p. 243.

$b+c = 2d$, then the capacity C_0 between the sphere and the planes is given by

(1) When $b = c$, $C_0 = a+(a^2/d)\log 2 = a+0{\cdot}693\,(a^2/d)$;*

(2) When $b = 2c$, $C_0 = a+0{\cdot}75\,(a^2/d)\log 3 = a+0{\cdot}819\,(a^2/d)$; and

(3) When $b = 3c$, $C_0 = a+1{\cdot}5\,(a^2/d)\log 2 = a+1{\cdot}040\,(a^2/d)$.

If there had only been one plane at a distance d from the centre of the sphere, this method gives us

$$C_0 = a+0{\cdot}5\,(a^2/d). \tag{35}$$

But by (29) the true value of C_0 in this case is

$$C_0 = a+F\left(a,\ \frac{a^2}{2d},\ \frac{a^2}{2d}\right).$$

Hence, when $a/d = 1/50$, we have to a seven figure accuracy

$$C_0 = a+\frac{a^2}{2d-a}. \tag{36}$$

In this case, therefore, the error introduced by using (35) instead of (36) is only about the hundredth part of 1per cent.

2. Let us consider the case of an infinite plane conducting sheet with a large hemispherical boss of radius b on it and let us find an approximate value of the capacity C_0 between this sheet and a small sphere of radius a whose centre coincides with the centre of the hemispherical boss. The image of the sheet in the sphere is a hemisphere of radius a^2/b.

Hence $$C' = 2\,(a^2/b)(1-1/\sqrt{3}) = 0{\cdot}845\,(a^2/b).\dagger$$

Hence we find that

$$C_0 = a+0{\cdot}845\,(a^2/b),$$

approximately.

The capacity between the small sphere and the hemispherical boss alone (the rest of the sheet being removed) would be given by

$$C_0 = a+(a^2/b)\left(\frac{1}{2}+\frac{1}{\pi}\right) = a+0{\cdot}818\,(a^2/b).\ddagger$$

If the sphere had been at the centre of a sphere of radius b, its capacity C_0 would be given by

$$C_0 = a+a^2/(b-a) = a+a^2/b \text{ approximately.}$$

We can write down in a similar way the capacity between a small sphere whose centre is on the axis of a long hollow cylindrical conductor, as the image in this case is an anchor ring, the capacity of which is known.* We can also write down at once an approximate value of the capacity between a tetrahedral or a cubical conducting sheet and a small sphere at its centre. In some cases, also, we can assume without appreciable error, that the capacity† of the image can be computed very approximately by the formula $(S/4\pi)^{\frac{1}{2}}$ where S is the surface of the image.

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* J. H. Jeans, 'Electricity and Magnetism,' Chap. VIII, ex. 41.

† W. D. Niven, 'London Math. Soc. Proc.,' vol. 8, p. 64; vol. 28, p. 205; H. M. Macdonald, *ibid.*, vol. 26, p. 156; vol. 28, p. 214.

‡ Kelvin, Reprint, p. 178; N. M. Ferrers, 'Quart. Journ.,' vol. 18, p. 97.

The Lateral Vibrations of Sharply-pointed Bars.

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In a preceding paper,‡ a discussion was given of the lateral vibrations of bars of circular cross-section formed by the revolution of the curve

$$y = Ax^n$$

—when n is between the values zero and unity—about the axis of x. The matter arose in connection with the siliceous deposits found upon a certain type of sponge spicule, as discussed in a joint paper by Prof. Dendy and the present author.§

It is of some interest to obtain a more extended knowledge of the vibrations of solids belonging to this class, with a view to further applications. The phenomena presented change in a curious manner with the value of n, and, in certain respects, could not be foreseen in an elementary way. A discussion of the subject, in numerical terms, for an exponent n between 1 and 2 is very laborious, and in the present paper we confine attention to the case $n = 2$. This is a limiting case, which presents very exceptional features, and gives rise to a period equation of an unusual type. It illustrates clearly, at the same time, the effect of sharpening the ends of the rod beyond the point at which they are conical ($n = 1$). The rod is a free-free bar, symmetrical about its axis, and each half is obtained by the revolution of a portion of a parabola about the tangent at its vertex.

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* F. W. Dyson, 'Phil. Trans.,' vol. 184, p. 43.

† A. Russell, 'Journ. Inst. of Elec. Engin.,' vol. 55, p. 12.

‡ 'Roy. Soc. Proc.,' A, vol. 93, p. 506 (1917).

§ 'Roy. Soc. Proc.,' B, vol. 89, p. 573 (1917).

When rotational inertia is neglected, the differential equation regulating the vibrations is

$$\mathrm{E}\frac{\partial^2}{\partial x^2}\left(\omega \mathrm{K}^2\frac{\partial^2 y}{\partial x^2}\right)+\omega\rho\frac{\partial^2 y}{\partial t^2}=0,$$

where y is the displacement at distance x from the end, E, and ρ are the modulus and density, ω is the sectional area, and K its radius of gyration about the appropriate axis. For a vibration of period $2\pi/p$,

$$\partial^2 y/\partial t^2 = -p^2 y,$$

and if the generating curve is $\eta = \mathrm{A}\xi^2$ we have

$$\omega = \pi \mathrm{A}^2 x^4, \qquad \mathrm{K}^2 = \tfrac{1}{4}\mathrm{A}^2 x^4,$$

whence

$$\frac{\partial^2}{\partial x^2}\left(x^8\frac{\partial^2 y}{\partial x^2}\right) = q x^4 y, \tag{1}$$

where

$$q = 4\rho^2/\mathrm{EA}^2. \tag{2}$$

If we use the operation $\vartheta \equiv x\dfrac{\partial}{\partial x}$ the equation becomes

$$\vartheta(\vartheta-1)(\vartheta+5)(\vartheta+6)y = qy$$

and the solution is

$$y = \mathrm{A}_1 x^{\alpha_1} + \mathrm{A}_2 x^{\alpha_2} + \mathrm{A}_3 x^{\alpha_3} + \mathrm{A}_4 x^{\alpha_4}$$

where the indices α are the roots of the biquadratic in m,

$$m(m-1)(m+5)(m+6) = q. \tag{3}$$

This case is, in fact, the only one in which the value of y is compounded of simple functions. The subsequent analysis of the periods recalls, in some respects, that of a similar problem of variable strings discussed by Lord Rayleigh, in that functions of the type $\cos(\beta\log x)$ are predominant.

Evidently, no vibrations are possible unless the equation (3) has two or four non-real roots, which can introduce trigonometric functions of $\log x$ into the value of y.

The quartic can be written in the form

$$(m^2+5m)(m^2+5m-6) = q,$$

whence

$$m^2+5m = 3\pm\sqrt{\{q+9\}}. \tag{4}$$

If

$$q+9 = (3+t)^2 \tag{5}$$

where t is essentially positive, the values of m ultimately become

$$m = -\tfrac{5}{2}\pm\tfrac{1}{2}\sqrt{\{49+4t\}}, \qquad m = -\tfrac{5}{2}\pm\tfrac{1}{2}\sqrt{\{25-4t\}}. \tag{6}$$

The first pair are necessarily real. The second pair cannot be complex unless t exceed $6\tfrac{1}{4}$, or q is greater than 76·5625. This gives a lower limit to the frequency of which the bar is capable under any conditions of support. This limiting case gives

$$\frac{p}{2\pi} = \frac{4{\cdot}375\,\mathrm{A}}{2\pi}\sqrt{\frac{\mathrm{E}}{\rho}}. \tag{7}$$

This frequency is seen later to be associated with a mathematically sharp end.

If this condition be satisfied, and if

$$(\alpha_1, \alpha_2) = -\tfrac{5}{2} \pm \tfrac{1}{2}\sqrt{\{49+4t\}}, \tag{8}$$

$$\gamma^2 = t - \tfrac{25}{4}, \tag{9}$$

then the value of y is

$$y = \mathrm{A}_1 x^{\alpha_1} + \mathrm{A}_2 x^{\alpha_2} + x^{-5/2}\{\mathrm{A}_3 \cos(\gamma \log x) + \mathrm{A}_4 \sin(\gamma \log x)\}. \tag{10}$$

Let the bar have a free end at $x = \epsilon$, where ϵ may be made small at a later stage. The shearing stress and bending moment at this point must vanish, so that, when $x = \epsilon$,

$$x^8 \frac{\partial^2 y}{\partial x^2} = 0, \qquad \frac{\partial}{\partial x}\left(x^8 \frac{\partial^2 y}{\partial x^2}\right) = 0. \tag{11}$$

We shall, as stated, illustrate the analysis only by a free-free bar, composed of two halves turned opposite ways, and joined at the greatest cross-section. Each is obtained by rotating the curve $y = \mathrm{A}x^2$, between $x = \epsilon$ and $x = l$, round the axis of x. The length of the bar is $2(l-\epsilon)$. We also limit attention to the symmetrical vibrations, in which the two ends are moving alike at any instant.

In such vibrations there is no shearing stress at $x = l$, and, moreover, dy/dx is zero by symmetry. These conditions, with (11), determine the period equation.

If $y = y_1 + y_2$, where

$$y_1 = x^{-5/2}\{\mathrm{A}_3 \cos(\gamma \log x) + \mathrm{A}_4 \sin(\gamma \log x)\}, \tag{12}$$

$$y_2 = \mathrm{A}_1 x^{\alpha_1} + \mathrm{A}_2 x^{\alpha_2}, \tag{13}$$

we find, with the use of the values of α, β, γ above that

$$\frac{\partial^2 y_1}{\partial x^2} = -\frac{6}{x}\frac{\partial y_1}{\partial x} - (\gamma^2 + \tfrac{25}{4})\frac{y_1}{x^2},$$

$$\frac{\partial}{\partial x}\left(x^8 \frac{\partial^2 y_1}{\partial x^2}\right) = -x^6(\gamma^2 + \tfrac{49}{4})\frac{\partial y_1}{\partial x},$$

$$\frac{\partial^2 y_2}{\partial x^2} = -\frac{6}{x}\frac{\partial y_2}{\partial x} + (6+t)\frac{y_2}{x^2} = -\frac{6}{x}\frac{\partial y_2}{\partial x} + (\gamma^2 + \tfrac{49}{4})\frac{y_2}{x^2},$$

$$\frac{\partial}{\partial x}\left(x^8 \frac{\partial^2 y_2}{\partial x^2}\right) = t x^6 \frac{\partial y_2}{\partial x} = x^6(\gamma^2 + \tfrac{25}{4})\frac{\partial y_2}{\partial x}.$$

Thus the conditions at the centre of the bar become

$$\frac{\partial y_1}{\partial x}+\frac{\partial y_2}{\partial x}=0,$$

$$(\gamma^2+\tfrac{49}{4})\frac{\partial y_1}{\partial x}-(\gamma^2+\tfrac{25}{4})\frac{\partial y_2}{\partial x}=0,$$

or, more briefly, $\partial y_1/\partial x$ and $\partial y_2/\partial x$ separately vanish when $x = l$. This is a considerable gain in simplicity. These conditions are satisfied by the form

$$y=\mathrm{H}\left\{\frac{x^{\alpha_1}}{\alpha_1 l^{\alpha_1}}-\frac{x^{\alpha_2}}{\alpha_2 l^{\alpha_2}}\right\}+\mathrm{K}x^{-5/2}\left\{2\gamma\cos\left(\gamma\log\frac{x}{l}\right)+5\sin\left(\gamma\log\frac{x}{l}\right)\right\}, \tag{14}$$

where H and K are arbitrary. This expression applies to any bar of this type vibrating symmetrically about its centre, whatever the conditions at the ends. For a free end at $x = \epsilon$ and at $x = 2l-2\epsilon$, the further conditions (11) become

$$(\gamma^2+\tfrac{25}{4})\frac{\partial y_2}{\partial x}=(\gamma^2+\tfrac{49}{4})\frac{\partial y_1}{\partial x},$$

$$6x\left(\frac{\partial y_1}{\partial x}+\frac{\partial y_2}{\partial x}\right)=(\gamma_2+\tfrac{49}{4})\,y^2-(\gamma^2+\tfrac{25}{4})\,y_1,$$

at $x = \epsilon$, where

$$x\frac{\partial y_2}{\partial x}=\mathrm{H}\left\{\left(\frac{\epsilon}{l}\right)^{\alpha_1}-\left(\frac{\epsilon}{l}\right)^{\alpha_2}\right\},$$

$$x\frac{\partial y_1}{\partial x}=-2(\gamma^2+\tfrac{25}{4})\,\mathrm{K}\sin\left(\gamma\log\frac{\epsilon}{l}\right)\cdot\epsilon^{-5/2}$$

on reduction. Thus using (18) below, by which

$$(\gamma^2+49)/(\alpha_1,\ \alpha_2)=5+\alpha_1,\ 5+\alpha_2,$$

we find ultimately

$$\mathrm{H}\left\{\left(\frac{\epsilon}{l}\right)^{\alpha_1}-\left(\frac{\epsilon}{l}\right)^{\alpha_2}\right\}=-2(\gamma^2+\tfrac{49}{4})\,\mathrm{K}\sin\left(\gamma\log\frac{\epsilon}{l}\right)\cdot\epsilon^{-5/2}, \tag{15}$$

$$\begin{aligned}\mathrm{H}&\left\{(\alpha_1-1)\left(\frac{\epsilon}{l}\right)^{\alpha_1}-(\alpha_2-1)\left(\frac{\epsilon}{l}\right)^{\alpha_2}\right\}\\&=(\gamma^2+\tfrac{25}{4})\left\{2\gamma\cos\left(\gamma\log\frac{\epsilon}{l}\right)-7\sin\left(\gamma\log\frac{\epsilon}{l}\right)\right\}\mathrm{K}\epsilon^{-5/2},\end{aligned} \tag{16}$$

and therefore

$$\gamma\cot\left(\gamma\log\frac{\epsilon}{l}\right)-\tfrac{7}{2}=-\left(\frac{4\gamma^2+49}{4\gamma^2+25}\right)\left\{\frac{(\alpha_2-1)-(\alpha_1-1)(\epsilon/l)^{\alpha_1-\alpha_2}}{1-(\epsilon/l)^{\alpha_1-\alpha_2}}\right\}. \tag{17}$$

This is the period equation. If the ratio ϵ/l is fixed, its solution gives the possible values of γ, and thence of the frequency, for α_1 and α_2 may be expressed in terms of γ by the equations (8, 9), which lead to

$$(\alpha_1,\ \alpha_2)=-\tfrac{5}{2}\pm\tfrac{1}{2}\surd\{74+4\gamma^2\}, \tag{18}$$

one being positive, and the other negative. Choose α_2 as the negative value and

$$\alpha_1 - \alpha_2 = \sqrt{\{74+4\gamma^2\}}, \tag{19}$$

which must be greater than 8. When ϵ is only comparatively small in relation to l, the ratio

$$\{(\alpha_2-1)-(\alpha_1-1)(\epsilon/l)^{\alpha_1-\alpha_2}\}/\{1-(\epsilon/l)^{\alpha_1-\alpha_2}\}$$

may be taken as α_2-1. For example, if the sectional area at one end of the rod is as much as one-quarter of the central sectional area, an error is involved only of magnitude 1 in 2^8 in the most unfavourable case. Thus the period equation may be reduced to

$$2\gamma \cot\left(\gamma \log\frac{\epsilon}{l}\right) - 7 = \left(\frac{4\gamma^2+49}{4\gamma^2+25}\right)\{7+\sqrt{(74+4\gamma^2)}\}. \tag{20}$$

Returning to (5) and (9), we notice that

$$q = (3+t)^2 - 9 = (\gamma^2 + \tfrac{37}{4})^2 - 9$$

and

$$q = 4\rho p^2/\mathrm{EA}^2,$$

where, if r_1 and r_2 are the radii of section at the end and at the centre,

$$r_1 = \mathrm{A}\epsilon^2, \qquad r_2 = \mathrm{A}l^2, \qquad \mathrm{A} = (\sqrt{r_2}-\sqrt{r_1})^2/(l-\epsilon)^2, \tag{21}$$

where $l-\epsilon$ is half the length of the rod. The frequency corresponding to any root γ of (20) is

$$\frac{p}{2\pi} = \frac{1}{16\pi}\sqrt{\frac{\mathrm{E}}{\rho}} \cdot \left(\frac{\sqrt{r_2}-\sqrt{r_1}}{l-\epsilon}\right)^2 \sqrt{\{(4\gamma^2+25)(4\gamma^2+49)\}}, \tag{22}$$

and in the period equation (20), $\log \epsilon/l$ may be replaced by $\frac{1}{2}\log r_1/r_2$.

Periods of the Rod.—The equation for γ may be written in the form

$$-\tan\left(\gamma \log\frac{l}{\epsilon}\right) = \frac{2\gamma(4\gamma^2+25)}{518+56\gamma^2+(4\gamma^2+49)\sqrt{(4\gamma^2+74)}}, \tag{23}$$

where the expression on the right is always necessarily real and positive, lying between zero and unity. Thus, for the first root of the equation, $\gamma \log l/\epsilon$ is an angle in the second quadrant, and, for the first vibration,

$$3\pi/4 < \gamma \log l/\epsilon < \pi,$$

while for the second

$$7\pi/4 < \gamma \log l/\epsilon < 2\pi$$

and so on, whatever be the value of the logarithm. As this logarithm increases, or the rod becomes sharper, the intervals between the frequencies of successive notes become shorter, all the values of γ tending towards zero. For an indefinitely sharp rod, with $\epsilon = 0$, we reach the curious conclusion that all the notes tend to the same frequency, which is the only frequency the bar can produce. A complete change in behaviour in this respect accompanies the passage from a double conical bar to one of the present type. This case could not, of course, be realised in practice, where, for a very sharp end, only a set of nearly equal frequencies would be obtained. The tendency to equality is only logarithmic.

When the ends are only fairly sharp, all the initial values of γ are small, and effectively given by

$$-\tan(\gamma \log l/\epsilon) = 0{\cdot}0532\gamma + 0{\cdot}00275\gamma^3, \tag{24}$$

whose solution, in a rapidly convergent form, is

$$\gamma = \frac{s\pi}{\log l/\epsilon} - \frac{0{\cdot}0532\, s\pi}{(\log l/\epsilon)^2} + \frac{0{\cdot}00283\, s^2\pi^2}{(\log l/\epsilon)^3} - \frac{0{\cdot}00285\, s^3\pi^3}{(\log l/\epsilon)^4} + \ldots, \tag{25}$$

obtained readily after the usual manner, where s takes integral values, excluding zero.

The limiting frequency corresponding to mathematically sharp ends is given by $\gamma = 0$ and $r_1 = 0$. It becomes

$$\frac{p}{2\pi} = \frac{35}{16\pi} \cdot \frac{r_2}{l^2} \cdot \sqrt{\frac{\mathrm{E}}{\rho}},$$

and is in fact the limiting frequency of which the bar is capable, as discussed in an earlier part of the paper (equation 7). When the ends are only moderately sharp, the frequency of the fundamental note, at least, approximates very closely to this value. It is dependent on the value of

$$\eta = \sqrt{\{(4\gamma^2+25)(4\gamma^2+49)\}}. \tag{26}$$

The values of η for the first three notes are exhibited in the following Table (Table I) for various degrees of sharpness of the rod:—

Table I.

	First note.		Second note.		Third note.	
$\mathrm{Log}_e l/\epsilon$.	γ.	$4\eta/35$.	γ.	$4\eta/35$.	γ.	$4\eta/35$.
4	0·775	1·072	1·549	1·286	2·319	1·633
5	0·620	1·046	1·241	1·1845	1·863	1·413
6	0·519	1·032	1·039	1·1295	1·556	1·289
7	0·445	1·024	0·890	1·095	1·336	1·213
8	0·390	1·018	0·780	1·073	1·170	1·164

This Table shows the slow convergence of η to the value 35/4. The higher the note, the slower is this convergence. We may use the formula

$$\frac{p}{2\pi} = \frac{35}{16\pi} \cdot \frac{\mathrm{R}\alpha}{\mathrm{L}^2} \sqrt{\frac{\mathrm{E}}{\rho}}, \tag{27}$$

for the frequencies, where

$$\alpha = \frac{4\eta}{35}\left(1 - \sqrt{\frac{r}{\mathrm{R}}}\right)^2, \tag{28}$$

and R, L are the central radius and semi-length of the bar, while r is the radius at the ends. Table II exhibits the values of α for various small values of the ratio r/R, or, in other words, the extent to which finite thickness at the ends is significant.

Table II.

	First note.	Second Note.	Third Note.
r/R.	α.	α.	α.
e^{-8}	1·033	1·239	1·574
e^{-10}	1·032	1·169	1·394
e^{-12}	1·027	1·124	1·283
e^{-14}	1·022	1·093	1·211
e^{-16}	1·017	1·072	1·163

It is evident that although the sharpness of the ends is not very important as a contributing factor to the fundamental frequency, which differs only slightly from its value for indefinitely sharp ends, when the end radius is only 1/3000 of that at the centre, the other frequencies are affected in a quite definite way, and are in fact very sensitive to the degree of sharpness as they recede from the fundamental. The limiting frequency would be very difficult to realise even approximately.

The Nodal Positions.—From (14) and (15), the vibration curve of the bar is of the form

$$y = \mathrm{K}x^{-5/2}\left\{2\gamma\cos\left(\gamma\log\frac{x}{l}\right)+5\sin\left(\gamma\log\frac{x}{l}\right)\right\}$$

$$-2\mathrm{K}\epsilon^{-5/2}\left(\gamma^2+\tfrac{49}{4}\right)\sin\left(\gamma\log\frac{x}{l}\right)\left\{\frac{x^{\alpha_1}}{\alpha_1 l^{\alpha_1}}-\frac{x^{\alpha_2}}{\alpha_2 l^{\alpha_2}}\right\}\Big/\left\{\left(\frac{\epsilon}{l}\right)^{\alpha_1}-\left(\frac{\epsilon}{l}\right)^{\alpha_2}\right\}, \quad (29)$$

where
$$(\alpha_1, \alpha_2) = -\tfrac{5}{2}\pm\sqrt{\left(\gamma^2+\tfrac{74}{4}\right)}$$

when ϵ/l is small, $(\epsilon/l)^{\alpha_1-\alpha_2}$ is less than $(\epsilon/l)^8$, and therefore negligible to a high order. The nodes are then given by

$$\left(\frac{x}{l}\right)^{-5/2}\left\{2\gamma\cos\left(\gamma\log\frac{x}{l}\right)+5\sin\left(\gamma\log\frac{x}{l}\right)\right\}$$

$$= 2\left(\gamma^2+\tfrac{49}{4}\right)\sin\left(\gamma\log\frac{x}{l}\right)\left\{\frac{x^{\alpha_1}}{\alpha_1 l^{\alpha_1}}-\frac{x^{\alpha_2}}{\alpha_2 l^{\alpha_2}}\right\}\left(\frac{\epsilon}{l}\right)^{-5/2-\alpha_2}. \quad (30)$$

Since x is less than l, and α_1 and α_2 are both numerically greater than unity, the expression on the right, multiplied by $(x/l)^{5/2}$, will not exceed $49(\epsilon/l)^4$, which is quite negligible even if $\log l/\epsilon$ is only about 3 or 4.

The nodal equation for a nearly sharp rod is thus reduced effectively to

$$\tan(\gamma \log x/l) = -2\gamma/5, \tag{31}$$

where γ itself is small. If γ tends to zero, the first root tends to

$$\log x/l = -\tfrac{2}{5}, \qquad x/l = e^{-2/5} = 0{\cdot}67032. \tag{32}$$

This corresponds to the limiting vibration, which thus has nodes at distances $0{\cdot}6703l$ from each end, where l is half the length.

We shall calculate the positions of the nodes for the first three notes in two other cases, in order to indicate the effect of sharpening the ends of the rod. The simple equation (31) may be used.

Case 1.—Log $l/\epsilon = 4$.

For the first three tones we have

$$\gamma = 0{\cdot}775, \quad 1{\cdot}549, \quad 2{\cdot}319,$$

$$2\gamma/5 = 0{\cdot}3100, \quad 0{\cdot}6196, \quad 0{\cdot}9276,$$

$$\log l/x = \gamma^{-1}\tan^{-1}(2\gamma/5) = 0{\cdot}3881, \quad 0{\cdot}3582, \quad 0{\cdot}3226.$$

These are the initial values in each case. More generally, $\pm s\pi/\gamma$ must be added, where s is an integer.

Thus for the *first tone*,

$$\log l/x = 0{\cdot}3881 \pm 4{\cdot}053s.$$

When $s = 1$, the positive sign gives $x < \epsilon$, lying outside the bar, and therefore an inadmissible value. The negative sign gives $x > l$, again inadmissible. There is thus, as we should expect, only one node, corresponding to

$$\log l/x = 0{\cdot}3881, \qquad x/l = e^{-0{\cdot}3881} = 0{\cdot}67834, \tag{33}$$

very close to the limiting node. A similar node exists in the other half of the bar.

For the *second tone*,

$$\log l/x = 0{\cdot}3582 \pm 2{\cdot}0265s.$$

There are two possible values, (a) corresponding to $s = 0$, and (b) corresponding to $s = 1$, with the positive sign in the ambiguity. These values are

$$x/l = e^{-0{\cdot}3582} = 0{\cdot}6989,$$

$$x/l = e^{-2{\cdot}3847} = 0{\cdot}0921, \tag{34}$$

where the first is near the critical value, and the second very close to the end of the rod. Two nodes would be expected in this vibration.

For the *third tone*,

$$\log l/x = 0{\cdot}3226 \pm 1{\cdot}3544s.$$

There are three possible values, as anticipated, corresponding to $s = 0, 1, 2,$

the positive sign being necessary in the two latter cases. The resulting values are

$$x/l = e^{-0\cdot3226} = 0\cdot7243,$$
$$x/l = e^{-1\cdot6770} = 0\cdot1869,$$
$$x/l = e^{-3\cdot0314} = 0\cdot0482, \qquad (35)$$

the third being still nearer to the end, and the first diverging further from the critical position.

CASE 2.—Log $l/\epsilon = 8$.

This corresponds to a much sharper rod. We find for the first three tones

$$\gamma = 0\cdot390, \quad 0\cdot780, \quad 1\cdot170,$$
$$\tan^{-1}(2\gamma/5) = 0\cdot1547, \quad 0\cdot3020, \quad 0\cdot4377,$$
$$\log l/x = 0\cdot3968 \pm 8\cdot0544s. \quad \text{(First tone.)}$$
$$= 0\cdot3877 \pm 4\cdot0277s. \quad \text{(Second tone.)}$$
$$= 0\cdot3741 \pm 2\cdot6851s. \quad \text{(Third tone.)}$$

The resulting possible nodes are, for the first tone,

$$x/l = e^{-0\cdot3968} = 0\cdot6725. \qquad (36)$$

For the second,

$$x/l = e^{-0\cdot3877} = 0\cdot6786,$$
$$x/l = e^{-4\cdot4154} = 0\cdot0121. \qquad (37)$$

For the third,

$$x/l = e^{-0\cdot3741} = 0\cdot6879,$$
$$x/l = e^{-3\cdot0592} = 0\cdot0469,$$
$$x/l = e^{-5\cdot7443} = 0\cdot0032. \qquad (38)$$

It is clear that, as the ends of the rod become sharper, all nodes, except one corresponding to each vibration, tend towards the ends of the rod. The higher the order of the note, the more rapid is this tendency. The exceptional node of each vibration tends to the limiting position, and the numerical cases discussed serve to make the process clearer. The conclusions are those which would be expected to accord with the behaviour of the frequencies.

An investigation of the unsymmetrical vibrations of the double rod of this type has also been made, but is much more complicated, and it is not thought necessary to reproduce it. We find, again, that the values of γ tend to zero when the rod becomes progressively sharper, and all the vibrations tend to have the limiting frequency. The central conditions here are $y = 0$ and $d^2y/dx^2 = 0$, for such vibrations involve a point of inflexion at the centre.

A similar problem presenting the same features is that of a single rod formed from the generating curve $y = Ax^2$, with the thick end clamped, and subject to the conditions $y = 0$, $dy/dx = 0$. But the peculiar form of the analysis in these cases has already been indicated sufficiently, together with the unusual acoustic behaviour of the systems derived from this particular generating curve.

With reference to the transition, through $y = Ax^n$, from the values $n = 1$, the limit of the preceding paper, and $n = 2$, the value in the present paper, it is necessary to point out that interpolation is not possible, and that the solution for intermediate values of n requires asymptotic formulæ, suitable for larger values of the argument, for the functions partially discussed in the first paper. These functions are of considerable interest and generality.

A New Method of Spectrophotometry in the Visible and Ultra-violet and the Absorption of Light by Silver Bromide.

By R. E. Slade, D.Sc., F.I.C., and F. C. Toy, B.Sc.

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Introduction.

A quantitative investigation of the absorption of light by silver bromide has been undertaken as a preliminary to a photochemical investigation of the action of silver bromide in the photographic dry plate.

A good summary of the advantages and disadvantages of the various methods which have been devised by different experimenters for the quantitative investigation of the absorption of light by substances is given by Ewest in a thesis entitled, "Beiträge zur quantitativen Spectralphotographie," of which an abstract is given by F. F. Renwick.[*] All the methods which have been used previously either depend upon Schwarzschild's law of the relation between time of exposure and the photographic effect, or a so-called neutral wedge is used which is supposed to absorb equally in all wave-lengths or is calibrated for selective absorption. The method which we have used is in some ways similar to that used by Ewest, but the apparatus required is very much simpler and a wedge of the material under examination is used instead of the neutral wedge of Ewest. In our method all that is required of the photographic plate is that the exposure of two adjacent portions of the same plate to the same light intensity of the same wave-length

[*] 'Photographic Journal,' vol. 54, p. 99 (1914).

or the same time gives the same density under identical conditions of development. This condition is easily satisfied. As will be seen in the sequel, errors are reduced to errors in measurements of length.

Method.

Consider a very thin wedge of the absorbing substance (fig. 1) with one face uniformly illuminated by parallel light incident normally.

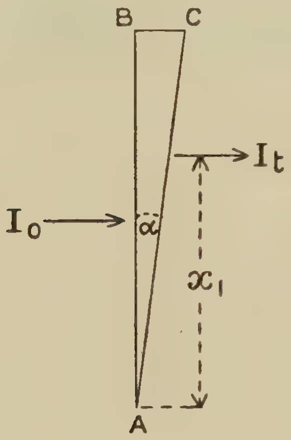

Fig. 1.

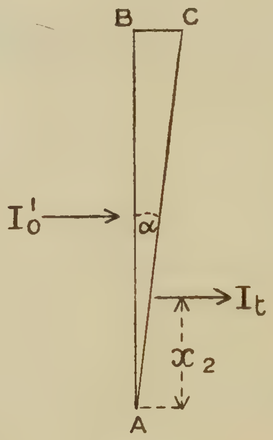

Fig. 2.

Let the uniform intensity incident on the face AB be I_0 and the intensity of the emergent light be I_t. I_t will vary along the length of the wedge, this variation being due only to the difference in thickness of absorbing medium traversed by the light, since reflection effects are identical at all points.

Neglecting the very small portions of I_t which is due to multiple reflection the relation of I_0 and I_t is given by

$$I_t = aI_0e^{-kd}, \tag{1}$$

where d is the thickness of the absorbing medium in centimetres, a is a factor depending on the amount of light reflected and k is the extinction coefficient.

Now let a uniform intensity I_0 produce an emergent intensity I_t at a distance x_1 from the thin end of the wedge (fig. 1).

If now I_0 is changed to I_0' ($I_0' < I_0$), at some new distance x_2 (fig. 2), there will be the same emergent intensity as before, since the decrease of incident intensity is balanced by the decrease in thickness of the absorbing medium.

We may therefore write

$$I_t = aI_0e^{-kd_1}, \qquad I_t = aI_0'e^{-kd_2},$$

$$\therefore \qquad I_0/I_0' = e^{k(d_1-d_2)}.$$

Whence we get, if α is the angle of the wedge,

$$k = \frac{\log_e (I_0/I_0')}{(x_1 - x_2) \cdot \tan \alpha}. \qquad (2)$$

The photographic plate is used to determine the distances x_1 and x_2 on the wedge. The wedge is placed at the slit of the spectroscope so that the intensity at any point, P, on the photographic plate is proportional to the intensity of the light which has passed through the wedge at the point of which P is the image. The two exposures for the same time, with incident intensities I_0 and I_0', are then taken side by side on the same plate, and the distances y_1 and y_2 (corresponding to x_1 and x_2 on the wedge) are determined in the following way.

Since the time of exposure has been the same in both cases and the plate and development are the same, the points on the plates which have been exposed to the same light intensity will have the same photographic density. We can determine such points and measure the difference of the distances of each from the image of the point of the wedge or from some arbitrary line such as the image of the end of the slit. Since it does not matter what density we use for comparison so long as we use the same density for both exposures, we found it convenient to use a density, such that on making a first positive then a second negative and finally a second positive (all on process plates) it was this density which just gave the sharp change from black to white in the second positive. On the developed negative the sharpness of change from black to white will depend on the value of k, the steepness of the wedge and the kind of plate used. Now, if a positive be made on another plate and preferably in parallel light, the resulting gradation may be made steeper, and though the distances y_1 and y_2 may change, they will change by the same amount in each case, the difference remaining constant. From the first positive a second negative and then a second positive may be made if necessary to obtain a sharp change from black to white. The distances y_1 and y_2 for each wave-length may then be measured directly by means of a travelling microscope.

In order to determine the distances x_1 and x_2 on the wedge corresponding to y_1 and y_2 on the plate, it is necessary to know the magnification at various wave-lengths produced by the optical system of the spectroscope. This can be done by placing an opaque object of known width across the jaws of the slit and comparing the width as obtained on the plate.

If $r = x/y$, where r is the reciprocal of the magnification, we have

$$k = \frac{\log_e I_0/I_0'}{(y_1 - y_2) \cdot r \cdot \tan \alpha}. \qquad (3)$$

The only condition necessary in regard to the time of exposure is that it shall be the same for the two exposures at intensities I_0 and I_0'. Exposures are therefore made sufficiently long for errors in the measurement of time to be negligible.

The wave-length may be found either by photographing a known spectrum on each side of the absorption spectra or on the top of the absorption spectra themselves. The latter method allows the wave-length to be determined at any point more quickly, and is quite satisfactory provided that the exposures are carefully regulated so as to show the lines only with clear glass as a background. By the use of suitable wedges the method is applicable to the measurement of extinction coefficients from values of the order of 1 to perhaps 100,000 or even more. This maximum is only limited by the smallest wedge which can be used and the intensity of the light source.

The Extinction Coefficient of Silver Bromide.

In determining the value of the extinction coefficient for silver bromide it was first necessary to prepare the salt optically clear. This was done as described by Lorenz and Eitel.* The wedge was made up between two similar optical plates of fused silica 1·9 cm. × 1·4 cm., prepared by Messrs. Adam Hilger, Limited. The high melting point of silver bromide (430° C.) prevented the use of quartz. The plates carefully cleaned, were placed in contact and held together as near one end as possible.

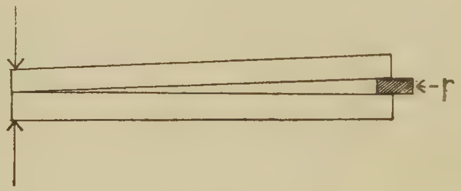

Fig. 3.

At the other end a flat piece of platinum foil, *p* (fig. 3), was inserted, the angle of the wedge depending on the thickness of the foil used. A portion of the silver bromide was remelted in a flat dish and the silica wedge, previously heated to about 500° C., lowered carefully into the dish until one edge just touched the surface of the liquid. Usually the liquid ran in by capillary attraction, but sometimes the wedge had to be reheated and the process repeated several times. When a satisfactory wedge was obtained it was allowed to cool slowly, care being taken to remove the platinum foil, just before the liquid solidified. If this was not done the bromide on contracting invariably broke away from the surface of the plates. The amount of contraction at any point is proportional to the thickness of the substance, *i.e.*, to the distance from the thin edge of the wedge, so that at all points the contraction tended to reduce the angle of the wedge by the same amount, so that the bromide on cooling did not become strained. When cold, the pressure on the end of the wedge was removed and the wedge kept in the dark till required for use.

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* 'Zeit. für Anorg. Chemie,' vol. 91, p. 57 (1915).

After the exposures had been made, the tangent of the angle of the wedge was determined by direct measurement with a travelling microscope.

In order to see the inside faces of the silica quite clearly, it was necessary to dissolve out the silver bromide just at the edge of the wedge by immersing in a solution of sodium thiosulphate. An example of values obtained for the tangent of the angle of one of the wedges used is given in Table A. Each value of the tangent measured was the mean of nine readings, and each set was taken at different distances along the wedge. For the case shown, the distance across the wide end of the wedge was 0·0772 mm. This was the smallest angle measured and was about 14 minutes. The instrument used for these measurements was made by Messrs. Adam Hilger, Limited, and read to 0·001 mm.

Table A.—Wedge No. 2.

Position.	Tan α.	Deviation from mean of single observation.
1	0·00420	8
2	0·00390	22
3	0·00408	4
4	0·00428	16
Mean......	0·00412	

Mean deviation of single observation = 0·00012.

$$\text{Average deviation of the mean} = \frac{0·00012}{\sqrt{4}} = 0·00006.$$

$$\therefore \quad \text{Tan}\ \alpha = 0·00412 \pm 0·00006.$$

No allowance was made for any slight curvature of the silica plates owing to the pressure applied at the thin end of the wedge. The error due to this would depend on the thickness of the plates and the magnitude and the point of application of the pressure. The silica plates were over 1 mm. thick and held as near the thin end as possible (fig. 3), so that the bending was very small, but to minimise any error due to this cause the first 2 mm. from the thin end were not used. For greater accuracy and for very small angles it would be necessary to make the wedge in such a way as to avoid the possibility of curvature. The wedges measured were considered accurate to less than 2 per cent.

The wedge was mounted in a small metal box, constructed to slide in the grooves for the slit cover of the spectroscope. The box was provided with a sliding cover, and had slits cut in the back and in the cover, so that, when the box was closed, the two slits were opposite. These slits were about 1 mm. wide, so that any strip of the wedge could be exposed at one time, the remainder being unexposed.

The inside face of the silver bromide should be in focus on the photographic plate, that is to say, it should be in mechanical contact with the slit. True gradation will then be rendered in the slit image. The distance of the bromide from the slit was about 1·5 mm. The error that this introduces will depend on the focal length of the collimating lens. For the spectroscope used the focal length of both lenses was large, being about 50 cm. Since both lenses had approximately the same focal lengths, we could determine the effect of this want of focus by removing the wedge and placing the plate out of focus the same distance as the wedge was during exposure, and finding what effect this had on the image of an opaque object placed in contact with the slit. Photographs were taken with one end of the plate 2 mm. out of focus. On the negative it was impossible to distinguish any difference in the sharpness of the edges of the opaque object. For smaller spectroscopes, where this want of focus is more important, owing to the shorter focal length of the collimating lens, we have found that it is possible, by dissolving out the bromide along the edge of the wedge, to remove one of the silica plates and place the inside face of the bromide in contact with the spectroscope slit.

The source of light used was a 50-volt half-watt metal filament lamp of 100 c.p. The filament was bent into a semicircle of about 0·75 cm. radius. The current for the lamp was obtained from an accumulator battery of 30 cells; an adjustable resistance was placed in the circuit and a voltmeter across the terminals of the lamp. The voltage could be kept constant to $\pm 0{\cdot}05$ volt. Assuming that the intensity of the source varies as the fifth power of the voltage, the maximum error introduced by the variation of the intensity is 1 per cent. All stray light was cut out by means of suitably placed stops.

The light intensity falling on the wedge was varied by moving the light source. The distances of the source of light from the wedge were in all cases sufficiently large to permit of the application of the inverse square law. The distances varied from about 1 to 2 metres, so that a maximum variation of intensity of about 1 : 4 was used. It is best to vary the ratio I_0/I_0' so as to keep (y_1-y_2) as large as possible. In this way we diminish both the errors in the ratio I_0/I_0' and in the measurement of (y_1-y_2). We were not able to vary the ratio I_0/I_0' as much as we should have wished, as the room in which we were working was not long enough for the light source to be more than 2 metres from the wedge. The plane of the filament was placed parallel to the plane of the slit, so that distances from all points of the filament to the slit could be considered equal. Distances were measured to the nearest 0·05 cm. Assuming an error of as much as 0·1 cm. in the measurement of each distance, the error in the ratio of intensities for distances of 100 cm. and 150 cm. works out at less than 0·5 per cent. Such large distances of the source of light from the slit were also necessary, in order that the intensity over the face of the wedge should be uniform, and that the whole of the light passing through the slit should fall on the collimating lens. A test was carried out for any variation of intensity on the plate due to want of parallelism of the jaws of the slit, but none could be detected with the fairly wide slit (0·15 mm.) which was used. A test was also made for interference effects, using water instead of the silver bromide in the wedge, but, with the wedges used, there was no variation of intensity which could be attributed to this cause.

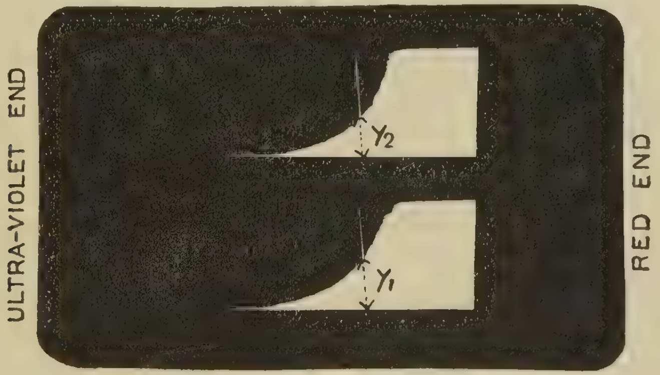

FIG 4.

WEDGE No 2. TIME OF EXPOSURE 90 MINUTES

$$\frac{I_0}{I_0'} = 3{\cdot}14.$$

The dotted lines shew y_1 and y_2 for $\lambda = 406{\cdot}3\ \mu\mu$.

Fig. 4 shows an example of a second positive made from an original negative in which the gradation extended over about 2 mm. The shape of the isopaque curve is determined by (1) k the extinction coefficient, (2) I_0 the intensity of the light, and (3) the sensitivity of the photographic plate. (The spectrum lines shown in fig. 4 are the violet lines of the copper arc, $\lambda = 402 \cdot 3\ \mu\mu$ and $\lambda = 406 \cdot 3\ \mu\mu$.) This second positive is sufficiently sharp to measure the distances y_1 and y_2 to $\pm 0 \cdot 01$ mm. Slight irregularities along the curve are due to small cracks and traces of impurity in the silver bromide wedge. The great advantage of using a continuous spectrum is that for reading at a bad point on the curve the correct position can be estimated by the eye from the shape of the curve on either side. At such a point the mean of several readings was taken, the difference between extreme readings being about 0·05 mm. At a good point on the curve the same value to 0·01 mm. was obtained at each reading. The distances $(y_1 - y_2)$ varied from 0·5 cm. to 0·075 cm. The maximum error, therefore, due to errors in measurements of these distances was of the order of 2·5 per cent. for the smallest values and became very small for large values. A test showed that the value of $(y_1 - y_2)$ was not affected by sharpening the original negative by successive printing. The same value, to within the accuracy of measurement, could be obtained from different positives made from the same original negative, but with different times of exposure. This shows that errors due to uneven coating of the plates are negligible.

With each wedge several different exposures were taken, the ratio I_o/I_o' being different in each case, so that for any given wave-length the values obtained for $(x_1 - x_2)$ varied also. The average value of $x_1 - x_2$ was of the order of 2 mm. An example of the results obtained is shown in Table B which gives the values of $\log_e I_o/I_o', (y_1 - y_2)$ and $(x_1 - x_2)$ for different photographs of the same wedge at $\lambda = 436 \cdot 5\ \mu\mu$, and the values of k as calculated from equation 3.

Table B.—Wedge No. 1 $\lambda = 436 \cdot 5\ \mu\mu$.

No. of photograph.	Time of exposure.	$\log_e I_0/I_0'$.	$y_1 - y_2$.	$x_1 - x_2$.	k.	Deviation of single observation from mean.
	min.		cm.	cm.		
1	10	0·577	0·133	0·127	480	22
2	5	0·577	0·140	0·135	450	8
3	3	1·227	0·287	0·275	470	12
4	3	0·837	0·209	0·200	430	28

Mean value of $k = 458$.
Average deviation of single observation = 18.
∴ Average deviation of the mean = 9.
∴ $k = 458 \pm 9$.

The following is an example of the way in which the value of k was determined for a single photograph. The example given is for photograph No. 2 in Table B.

$$\lambda = 436{\cdot}5\,\mu\mu. \quad \text{Exposure} = 5 \text{ minutes.}$$

Values of y_1 (cm.). 0·461, 0·460, 0·461, 0·461. Mean $y_1 = 0{\cdot}461$ cm.

Values of y_2 (cm.). 0·321, 0·322, 0·321, 0·320. Mean $y_2 = 0{\cdot}321$ cm.

$$\therefore \qquad y_1 - y_2 = 0{\cdot}140 \text{ cm.}, \qquad r = 0{\cdot}965,$$

$$\therefore \qquad x_1 - x_2 = (0{\cdot}965) \times (0{\cdot}140) = 0{\cdot}135 \text{ cm.},$$

$$\tan \alpha = 0{\cdot}00950.$$

Distances of light source from wedge = 106·9 cm. and 142·8 cm.

$$\therefore \qquad \mathrm{I}_0/\mathrm{I}_0' = \left(\frac{142{\cdot}8}{106{\cdot}9}\right)^2 = 1{\cdot}78.$$

$$\therefore \qquad \log_e \mathrm{I}_0/\mathrm{I}_0' = 0{\cdot}577,$$

$$\therefore \qquad k = \frac{0{\cdot}577}{(0{\cdot}135) \times (0{\cdot}00950)} = 450.$$

The value of k was determined on each plate for points 1, 2, 3, etc., millimetres from the copper line $\lambda = 402{\cdot}3\ \mu\mu$.

These distances were measured on the Vernier scale of a microscope mechanical stage which was fixed on the stage of the travelling microscope used to measure y_1 and y_2. This mechanical stage could only be read to 0·1 mm. and estimated to 0·025 mm. This was quite accurate enough for determining the wave-length to 1 $\mu\mu$, but if the isopaque curve was steep it is obvious that an error in the position at which the value of y was measured would cause an error in the value of y. But the steeper the isopaque the greater the difference $(y_1 - y_2)$, so that it is not necessary to measure y with so much accuracy in this case. No measurements were made, however, on the steepest portion of the isopaque curves.

The value of the reduction factor r (where $r \times y = x$) was obtained for several wave-lengths and a smooth curve drawn. It varied from 0·955 at $\lambda = 460\ \mu\mu$ to 0·980 at $\lambda = 350\ \mu\mu$. The length of the opaque object measured was about 0·7 cm., so that the error in the value of r was very small, and could be neglected.

The points plotted in fig. 5 are the average values of k obtained at each wave-length with different wedges. It will be seen that the values obtained with the two measured wedges for the same wave-lengths are in very fair agreement. The angle of the thinnest wedge No. 3 was not measured, but calculated from the values of k, at certain wave-lengths, which had been determined with one of the other wedges (No. 2).

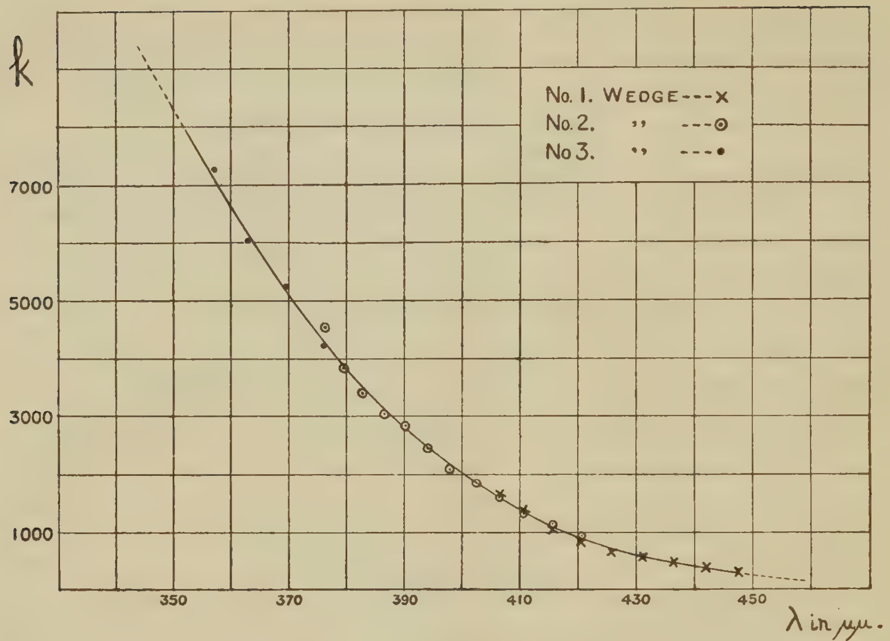

Fig. 5.

Table C.

λ.	k.	λ.	k.
μμ.		μμ.	
450	270	400	2000
440	410	390	2790
430	600	380	3800
420	900	370	5100
410	1380	360	6700

In Table C are given the values of k as read off from the smooth curve at intervals of $10\mu\mu$. To obtain a check on these figures an approximate value of k was determined in the visible spectrum for the blue mercury lines (mean $\lambda = 434{\cdot}7\mu\mu$) by means of a Konig-Martin spectrophotometer, and a value of $k = 530$ was obtained. The value as read off the curve is 510.

The average errors of the mean values of k which are plotted in fig. 5, vary from 1·5 to 4·5 per cent. These were calculated as in Table B. From these values it is estimated that the average error of any of the values given in Table C is less than 3 per cent. In this, of course, only the variable part of the error is included, but the constant error has been eliminated as far as possible by the variation of the conditions under which the different observations were made. We believe that the greatest constant error is that of the instrument which has been used in the measurement of the lengths.

Further Experiments on the Variation of Wave-length of the Oscillations Generated by an Ionic Valve due to Changes in Filament Current.

By J. H. Vincent, M.A., D.Sc.

(Communicated by Prof. W. H. Bragg, F.R.S. Received February 19, 1920.)

Introduction.

In the course of a research* on the effects produced on the wave-length of the oscillations given out by a triode maintained oscillator when various changes were made in the circuit, Eccles and Vincent showed that in an oscillatory circuit maintained by a B valve with a grid coil coupling (like the two oscillatory circuits in fig. 1) the wave-length varies slightly with the filament current and has a maximum value for a certain filament current. In all cases investigated it was found possible so to adjust the coupling between the grid coil and main oscillator coil as to allow the filament current to be set to make the wave-length a maximum.

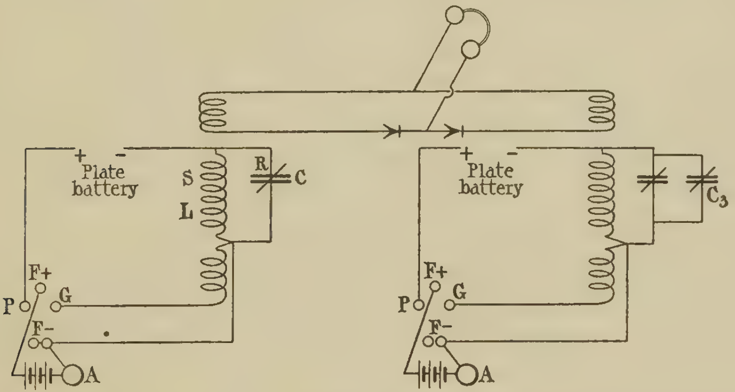

Fig. 1.

Elimination of Possible Effects of Self-induction in the Filament Circuit.

Experience gained in dealing with oscillatory circuits had emphasized the difficulty and importance of avoiding changes in other variables of a circuit when it is desired to study the effects due to the alteration of some one variable. In the former work the changes in the filament current have been brought about by adjusting a rheostat in which the motion of the slider altered the portion of a solenoid included in the filament circuit. The self-induction of the filament circuit was thus altered as well as the resistance and it was quite conceivable that the change in the inductance might have some effect. Experiments were carried out in which the variable resistance consisted merely of an electric arc carbon, 27 cm. long and 0·5 cm. in diameter having a resistance of about 1·2 ohms. One end of this was copper plated and soldered to a wire while the sliding contact consisted of a spring of copper. The wave-length was again found to have a maximum value for a definite filament current. In this experiment, however, the self-induction of the filament circuit was not absolutely constant, for the contour of the circuit is appreciably altered by the motion of the slider. An arc carbon rheostat was then made in which the contour of the circuit is very little varied by the motion of the slider.

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* Eccles and Vincent, 'Roy. Soc. Proc.,' A, vol. 96 (1920).

The Arc Carbon Rheostat.

This consists of an arc carbon mounted on a vertical side of a horizontal brass bar of square cross section. The carbon is supported mechanically by cementing it to a strip of vulcanised fibre which in turn is cemented to the vertical side of the brass bar. The carbon may be either mounted unprepared or it may have its resistance very materially increased by carefully grinding and filing. Before mounting the carbon rod or strip, one end is copper plated and soldered to a wire which is connected to one of the terminals of the rheostat. The other terminal is in electrical connection with the brass bar and with a horizontal brass rod vertically under it upon which the slider sits. The spring of the slider forces a blunt metal knife edge against the carbon and the reaction is taken by the other side of the brass bar. A current entering by one terminal traverses the brass rod and bar to the slider, passes along the rest of the carbon to the copper-plated end and hence to the other terminal of the rheostat. By the use of this rheostat sufficient variation in current may be obtained to draw a filament current wave-length curve while the variation in the self-induction of the filament current circuit is sensibly constant.

In fig. 2 is shown the small portion of the curve when the filament current varies from about a fiftieth of an ampère below to a fiftieth of an ampère

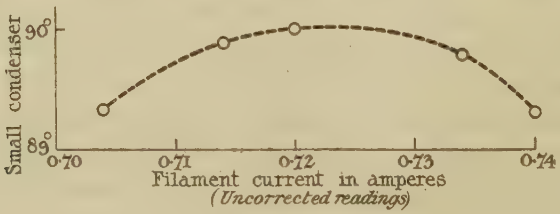

FIG. 2.

above the current for which the wave-length is a maximum. The whole change in the ordinates represents a change in wave-length of 22 cm. the wave-length being about 3000 metres. A larger part of the curve is shown in fig. 3, which was obtained by using a thinner strip of arc carbon in the rheostat. The vertical scale of this figure is the same as in the last one, a degree of the small condenser (C_3, fig. 1) corresponding to a third of a metre in the wave-length.

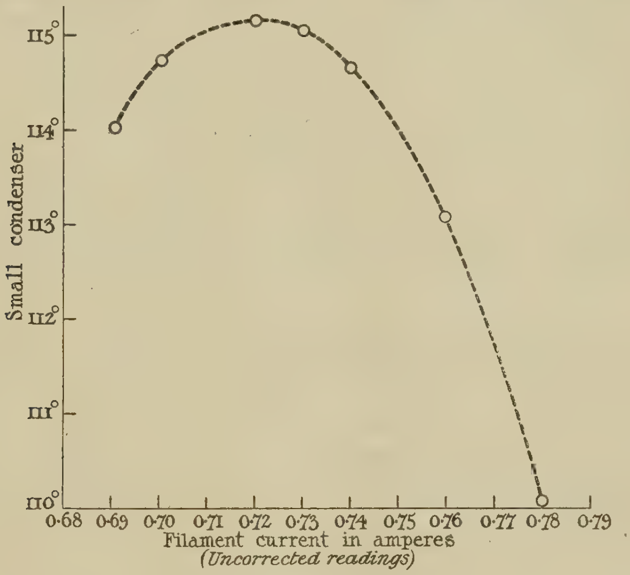

Fig. 3.

Use of Different Methods of Linking and Rectifying.

The results given by Eccles and Vincent and those already described above have been obtained by employing the differential wave meter described in the former paper. In this apparatus the linking circuit consisted of two coils connected merely by leads. (To avoid circumlocution, a third circuit influenced electro-magnetically by two main oscillatory circuits of a differential wave meter is called a linking circuit.) Each one of these coils was placed near one of the main oscillator coils while the telephone was inserted in the plate battery circuit of one of the oscillator sets and was shunted with a condenser. This oscillating circuit had its main condenser shunted by a variable condenser of small capacity (as C_3, fig. 1) the readings of which combined with the constants of the circuits enable small changes in the wave-length to be measured. There are two objections to this form of linking and rectification. The first is that the electromagnetic coupling of the two main circuits is liable to introduce trouble. The effective coupling was reduced by inserting a crystal detector in the linking circuit. The second objection is that the arrangement was unsymmetrical. The telephone and its shunting condenser were removed from the plate circuit and the telephone was put in the linking circuit in series with the crystal detector and the two coils. Curves giving the change of wave-length with filament current were drawn and were found to be of the same character as those previously obtained. The note in the telephone was not as loud as before, but the intensity increased considerably on shunting the telephone with a condenser.

By using two crystal detectors in series in one of the leads connecting the linking coils, and joining up the telephone to a point between these detectors and the other lead, a sufficiently loud note is obtained without shunting the telephone with a condenser. The whole differential wave meter, as now arranged, is shown diagrammatically in fig. 1, in which the two carborundum brass detectors are shown joined up in the same sense in one of the leads of the linking circuit. It was found that reversing the connections of one of the detectors made no difference. Whether this method of linking and rectifying is better than that used in the previous work is not certain. The note in the telephone was not quite as loud as in the original arrangement, unless the linking coils were placed nearer the oscillating coils, so that it may be that the gain in electromagnetic freedom is at the expense of increased electrostatic coupling. But the point at present is that the arrangement provides a third method of linking and rectifying, which can be used to test the legitimacy of the earlier results. Curves drawn with this apparatus were similar to those already obtained, so that we may regard the existence of a maximum wave-length for a particular current as a genuine effect, independent of the method by which the change in wave-length is studied.

Filament Current Wave-length Curves of Different Valves.

Several valves, but all of the B type, have been tested. In all cases it has been found possible to adjust the mutual induction of the grid coil and main oscillator coil, so that the maximum wave-length is given when the filament current has a value which enables the valve to maintain the oscillations. The actual shape of the curve is a function of the valve and of the circuit in which it works, but the typical curve rises very slowly at first as the filament current is increased, then becomes steeper until the maximum is approached; the curve ends abruptly on its descending side, when the current in the filament passes a certain value. In one valve the initial portion of the curve shows a distinct but slight bend towards the axis of the current: with this valve a minimum wave-length is obtainable in addition to the usual maximum.

Amplitude and Wave-Length.

It is, of course, well known that, as the filament current is gradually raised from a very small value, the oscillations cannot be detected until a definite filament current is reached, and that the amplitude of the oscillations at first increases as the current rises. This rise in current is accompanied by an increase in wave-length. When the current in the filament of a B valve is raised above a certain value, the intensity of the oscillations falls. We have seen that the wave-length also decreases. When the conditions are arranged so as to get the maximum wave-length on an accessible part of the filament current axis, the maximum amplitude is probably given by the same current as yields the maximum wave-length. This last statement is made on the strength of experiments in which the amplitude is assumed to be proportional to the readings of a galvanometer in series with a crystal detector shunting the condenser of a resonating circuit.

Other cases in which the amplitude and wave-length seem to be correlated are when the resistance of either of the branches R or S (fig. 1) is changed. Increasing either, lessens the amplitude and decreases the wave-length. The experiments on this point are not yet published.

We have, then, seven cases, which can be connected together by the following rule :—When any one of the changes below is made in a valve set of the type of those in fig. 1, worked by B valves, the wave-length and amplitude decrease.

1. Decrease grid voltage.
2. Decrease plate voltage.
3. Decrease grid coil coupling with main oscillator coil.
4. Increase resistance in condenser branch of oscillator circuit (R, fig. 1).
5. Increase resistance in self-induction branch of oscillator circuit (S, fig. 1).
6. Increase the filament current beyond the value which gives the maximum wave-length.
7. Decrease the filament current below this value.

At present, the writer suggests the above rule merely as a useful aid in remembering the sign of the effect on the wave-length of these changes in the circuit. The effect on the amplitude can in general be deduced by imagining the change pushed to the extreme limit, and then the above rule enables one to find the sign of the consequent change of the wave-length. No claim is put forward that the curves giving the simultaneous values of the wave-length and amplitude are parallel or have absolutely coincident maxima, but it seems probable that there is a close connection between them which will be disclosed by further experiments.

The work described above was carried out in Dr. Eccles' laboratory, under his direction and at his suggestion. I wish to thank him for having initiated me into the use of the apparatus, and for constant help and advice during the progress of the research.

On a Theory of the Second Order Longitudinal Spherical Aberration for a Symmetrical Optical System.

By T. Y. Baker, Instructor Commander R.N.; and L. N. G. Filon, M.A., D.Sc., F.R.S., Goldsmid Professor of Applied Mathematics and Mechanics in the University of London.

(Received December 2, 1919.)

(Abstract.)

1. The object of this investigation is to establish a formula for the longitudinal spherical aberration of rays which traverse a symmetrical optical system in an axial plane that shall be capable of fairly easy computation for any combination of lenses, and at the same time shall be accurate to the second order and free from certain important difficulties of convergency which occur in certain neighbourhoods when we attempt to use for the longitudinal aberration the method of aberration of successive orders.

From the point of view of the optical designer, the usual theory of aberrations, which, for all practical purposes, is largely restricted to the first order, is known to give an unsatisfactory approximation. In practice, the designer adopts a semi-empirical method of tracing a number of rays through the system by means of the trigonometrical equations, a method which is laborious and lengthy, and which can at best give only incomplete information and very limited guidance for effecting improvements.

2. The type of formula established in the present paper was originally suggested by an empirical formula discovered by the authors* when trying to fit the aberrations of a series of thick lenses, obtained from the ray paths calculated trigonometrically. This formula, when tested, fitted the results

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* 'Transactions of the Optical Society,' December, 1918.

with surprising closeness, well beyond the accuracy of the ordinary series of aberrations, even when the second order was included.

The justification of it on mathematical grounds was not, however, obvious, and it was some time before the authors were able to establish it. This justification is given in the present paper.

3. After a description of the notation the question of convergency of the series of aberrations is discussed. It is shown that when the magnification exceeds numerically a certain limit the functions represented by the series of aberrations of successive orders may possess not only poles but branch-points, and that in a critical neighbourhood the range of validity of the developments dwindles to zero. These characteristics are shown to depend, not only upon the object and image positions and the curvatures of the refracting surfaces, but upon the argument in powers of which the development is made, in particular according as the developments proceed in ascending powers of trigonometrical functions of the emergent, or of the incident, inclination of the ray to the axis of the optical system. It is proved that developments in terms of the *incident* inclination α_0, or, what amounts to the same thing, of the slope of the "Gaussian" emergent ray, are free everywhere from branch points within a fixed finite radius, and have in general a more rapid convergence than developments in terms of the actual *emergent* inclination α.

4. The formula for the longitudinal aberration which is discussed in the present paper is of the type

$$\frac{\mathrm{A}t^2}{1+\mathrm{B}t^2}.$$

where t is the slope of the emergent ray calculated by Gauss' method, A is the usual coefficient of first order aberration, and B is another coefficient, of which the value is found.

The coefficients A and B are polynomials in the magnification, A being of degree four and B of degree three. This formula is shown to be correct as far as the second order inclusive for a single refracting surface. For a single lens it requires to be supplemented by an additional term $\mathrm{E}t^4$ in the numerator, where E is a polynomial of sixth degree in the magnification. Calculation shows that this additional term, in the majority of cases, is of slight importance, at any rate for a single lens.

5. A parallel formula is found for the well-known "sine-ratio," viz.:

$$\frac{\sin \alpha_0}{\sin \alpha} = \mathrm{M}\left(\frac{1+\mathrm{C}'t^2}{1+\mathrm{B}t^2}\right),$$

where M is the paraxial sine-ratio and $t = \tan \alpha_0/\mathrm{M}$. This formula holds good as far as the second order for the single refracting surface. In the more general case we have

$$\frac{\tan \alpha_0}{\tan \alpha} = \mathrm{M}\left(\frac{1+\mathrm{C}t^2}{1+\mathrm{B}t^2}\right),$$

where the formula holds as far as the *first* order of aberrations only; the *second* order of aberrations for the *inclinations* of the rays not being required for our present purpose.

The coefficients C and C′ above are found to be quadratics in the magnification, and the second formula, although on development it gives $\tan \alpha / \tan \alpha_0$ correct only as far as t^2, generally leads to a much improved numerical determination of the inclination.

6. The paper goes on to show how formulæ of similar type can be established for a combination of two or more systems, and how to obtain the A, B, C, E for the combined system in terms of the partial A, B, C, E's and the partial magnifications. It is found that the partial coefficients for each of the component systems enter into the equations of combination *linearly*, so that the contribution of any lens, or groups of lenses, to the total aberration can be readily isolated.

7. Certain important invariant relations, independent of the number and shape of the refracting surfaces and connecting the quantities A, B, C, E, and also the corresponding quantities for the same optical systems reversed, are proved.

8. Finally, explicit expressions for A, B, C, E for both thick and thin lenses, in terms of the focal length and the two curvatures, are given for reference.

9. Stress is laid on the closeness of fit of the formula wherever it has been found possible to test it. This closeness of fit appears to go beyond mere accuracy to the second order, and suggests that progress in the algebraic treatment of the aberrations of a symmetrical optical instrument may well be looked for, not so much along the line of development in series, but in other mathematical directions, such as continued products or possibly continued fractions.

A New Apparatus for drawing Conic Curves.

By A. F. Dufton, B.A., Trinity College, Cambridge.

(Communicated by Prof. C. V. Boys, F.R.S. Received February 21, 1920.)

1. The attention of mathematicians has been attracted to the mechanical description of conic sections since the discovery of the curves by Menæchmus, but in the numerous mechanisms which have been invented only partial success has been attained.

In an early conograph, the invention of which is ascribed to the Arabs, the curve is the actual intersection of the surface upon which it is drawn with a straight line generating a cone. Instruments of this kind were designed at the end of the sixteenth century for use in the construction of sundials.

Newton, in his 'Principia,'* discusses the drawing of conic sections and describes a mechanical method of plotting them. Two angles are rotated about their vertices and the intersection of one pair of arms is kept upon a fixed straight line. The locus of intersection of the other pair is a conic section.

Sylvester† showed that a conic can be drawn by means of an apparatus of thirteen links. His method fails to draw the curve at the vertex but is simpler than that of Peaucellier,‡ which involves the use of fifteen links besides a cross-piece rigidly attached to one of them. Both these methods depend upon the principle of inversion.

A conograph based upon the constancy of the anharmonic ratio subtended at the tracing point by four fixed points on the curve was invented by Willy Jürges.§ In this instrument the use of eight sliding constraints makes smooth working difficult.

2. With the apparatus described in this paper, the conic is drawn as the polar reciprocal of a circle. The circle to be reciprocated, of centre O and radius ON, is enveloped by a straight line AB. The points A and B lie upon a fixed straight line at a distance ON from O and the paper containing the circle is rotated about O. To the paper is fixed, at the centre of reciprocation, which becomes a focus of the conic, the joint S of a four-bar linkage. Two equal bars SC and SD are hinged to the middle points C and D of equal bars ACP and BDP hinged together at P. This linkage has the property that P

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* 'Principia,' Lib. I, Prob. XIV.

† 'Proc. Roy. Inst.,' vol. 7, p. 179 (1873–75).

‡ *Ibid.*

§ 'Zeitschrift für Mathematik. und Physik.,' vol. 38, p. 350 (1893).

is the pole of AB with respect to a circle of centre S and radius $(SC^2-CP^2)^{\frac{1}{2}}$. For, if PK and CM be perpendicular to AB and SP respectively,

$$SK,\, SP = (SM-KM)(SM+MP) = SM^2-MP^2 = SC^2-CP^2.$$

P therefore describes upon the paper the polar reciprocal of the circle of

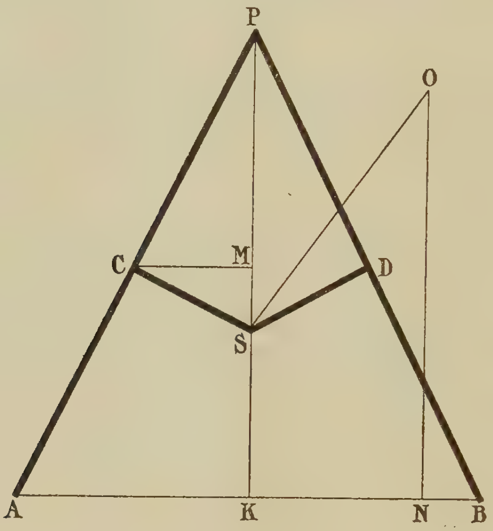

Fig. 1.

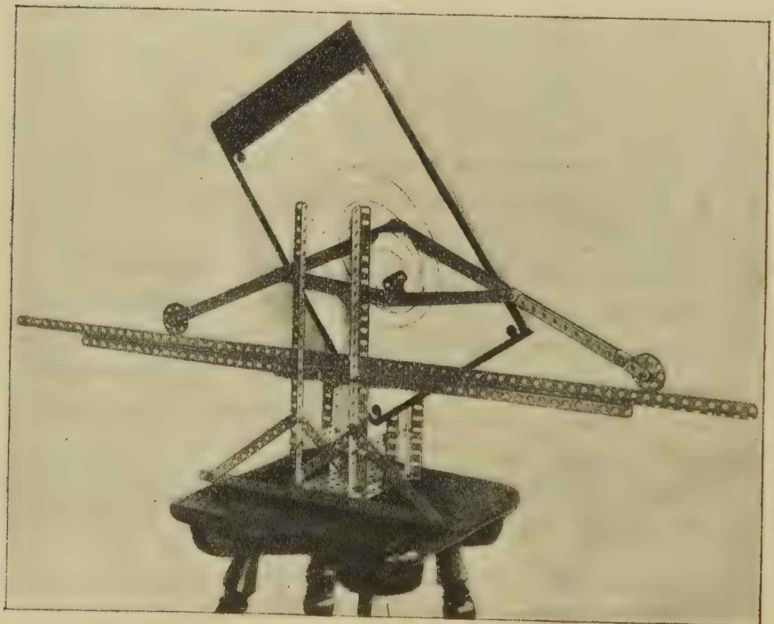

Fig. 2.

centre O and radius ON, that is a conic with focus S, axis SO, eccentricity OS/ON and latus rectum $2(CP^2-SC^2)/ON$.

3. The first model of the apparatus, constructed of "Meccano," is shown in fig. 2. Wheels, running upon a horizontal rail, constrain the points A and B. The axis of the hinge P is a glass tube which, drawn to a point, serves as the drawing pen. The paper is pinned to a drawing board, which can rotate in its own plane about a horizontal axis supported upon friction wheels. As the board is rotated the pen traces upon the paper.

The latus-rectum, which depends upon the length ON, can be varied by vertical adjustment of the rail. The eccentricity, OS/ON, of the conic is determined, when the rail is fixed, by the "eccentricity," OS, of the focus from the axis of rotation.

The curves shown in fig. 3 were drawn with this model. In the remarkable precision of even a roughly made instrument, in the tracing of the curve at one sweep and in the application to all conics from circle to straight line, the apparatus offers a satisfactory solution to a very ancient problem.

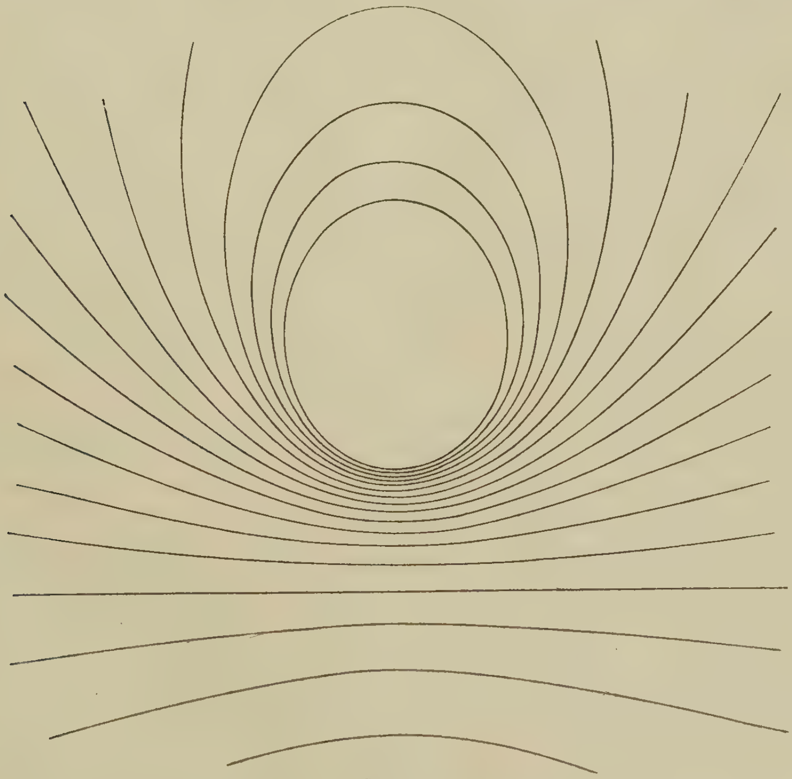

FIG. 3.

The Pressure Distribution on the Head of a Shell Moving at High Velocities.

By L. Bairstow, F.R.S., R. H. Fowler, and D. R. Hartree.

(Received December 12, 1919.)

§ 1. *Introduction.*—The pressure at any point of a body moving through a fluid may be considered to consist of two components—*the static pressure*, which would be the pressure at that point, if there were no relative motion between the body and the fluid—and *the dynamic pressure* due to the relative motion. The sum may be called *the total pressure* at the point, and is, of course, always positive; the dynamic pressure alone may be negative.

Experiments, of an introductory kind, were undertaken by the authors, at the request of the Ordnance Committee, to attempt to determine, as a function of the velocity of the shell, the dynamic pressure at various points on the head of a shell, whose axis of symmetry and direction of motion coincide or nearly coincide. The results appear to be not without general scientific interest, and are therefore presented in this paper by permission of the Ordnance Committee. The authors' best thanks are due to the officers of the Experimental Department, H.M.S. "Excellent," on whose range the firing trial was carried out; to the other officers of the Munitions Inventions Department, who shared the work of observation and computation; to the Director of the National Physical Laboratory, where the comparative observations at low velocities were made in a wind channel; and, above all, to Mr. W. J. Goudie, of University College, London, on whose determinations of the rates of burning of powder-train time-fuzes at high rotational speeds the whole experiment was based.

The fundamental idea of the experiments is the use of a service time-fuze as a manometer to determine the pressure under which the powder is burning.*

The rate of burning of a service time-fuze is known from laboratory experiments to be affected by the total external pressure on the vents. Let us assume for the moment that this is the only factor that influences the rate of burning. A series of observations, for shells fired along the same trajectory at short intervals of time, determines a relation between time of burning and length of fuze burnt. By numerical differentiation of the observations, we can obtain a relation between the rate of burning and the time, *and therefore, by comparison with the laboratory experiments, between the external pressure and the time.* If the circumstances of the shell's motion are known, this leads at once to a relation between the dynamic pressure on the fuze vents and the time, and so to the required relation between the dynamic pressure, the velocity of the shell, and the prevailing atmospheric conditions.

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* A service time-fuze contains a train of gunpowder, which is ignited by a detonator pellet on the shock of discharge from the gun. The "setting" of the fuze can be varied so that a length of powder train depending on the setting is burnt before the magazine of the fuze is ignited and the shell exploded. The setting is specified by a number which defines the length of composition burnt on an arbitrary scale. The time of burning is taken as equal to the time interval between the firing of the gun and the bursting of the shell.

The external total pressure is not the only factor that affects the rate of burning. Under identical physical conditions, the rate of burning varies from batch to batch of powder; it is largely affected by the spin of the shell, and is sometimes appreciably dependent on the temperature of the fuze mixture. In spite of these effects, however, it became increasingly clear, as experience of time-fuzes increased, that, with suitably designed control experiments to determine the rate of burning of the fuze in the proper physical conditions, a time-fuze could be used as a manometer to determine rough quantitative values of the external pressure during the flight of a shell.

§ 2. *General Scheme of an Experiment Based on the Fuze Manometer.*—In the application described in this paper, shells were fitted with caps entirely enclosing the fuze; each cap had a series of holes drilled in it at the same distance from the nose (fig. 1). The external pressure on the vent holes of the fuze is the pressure inside the cap; the latter pressure is practically equal to that immediately outside the hole (see § 8). Proceeding as described in § 1, we can obtain a relation between the pressure inside the cap and the velocity of the shell along a given trajectory, for a given position of the ring of holes.

On the assumption that the presence of a hole has an unimportant effect,* we can determine the pressure-velocity relation for a series of points on the head of a shell by using caps with rings of holes at a series of positions, and draw curves (fig. 2) showing the variation with velocity of the dynamic pressure at a given point. For any given velocity we can draw curves (fig. 3) showing the distribution of dynamic pressure over the head of the shell. By integrating these dynamic pressures, we can deduce the contribution to the drag due to the dynamic pressure on the head of the shell. The

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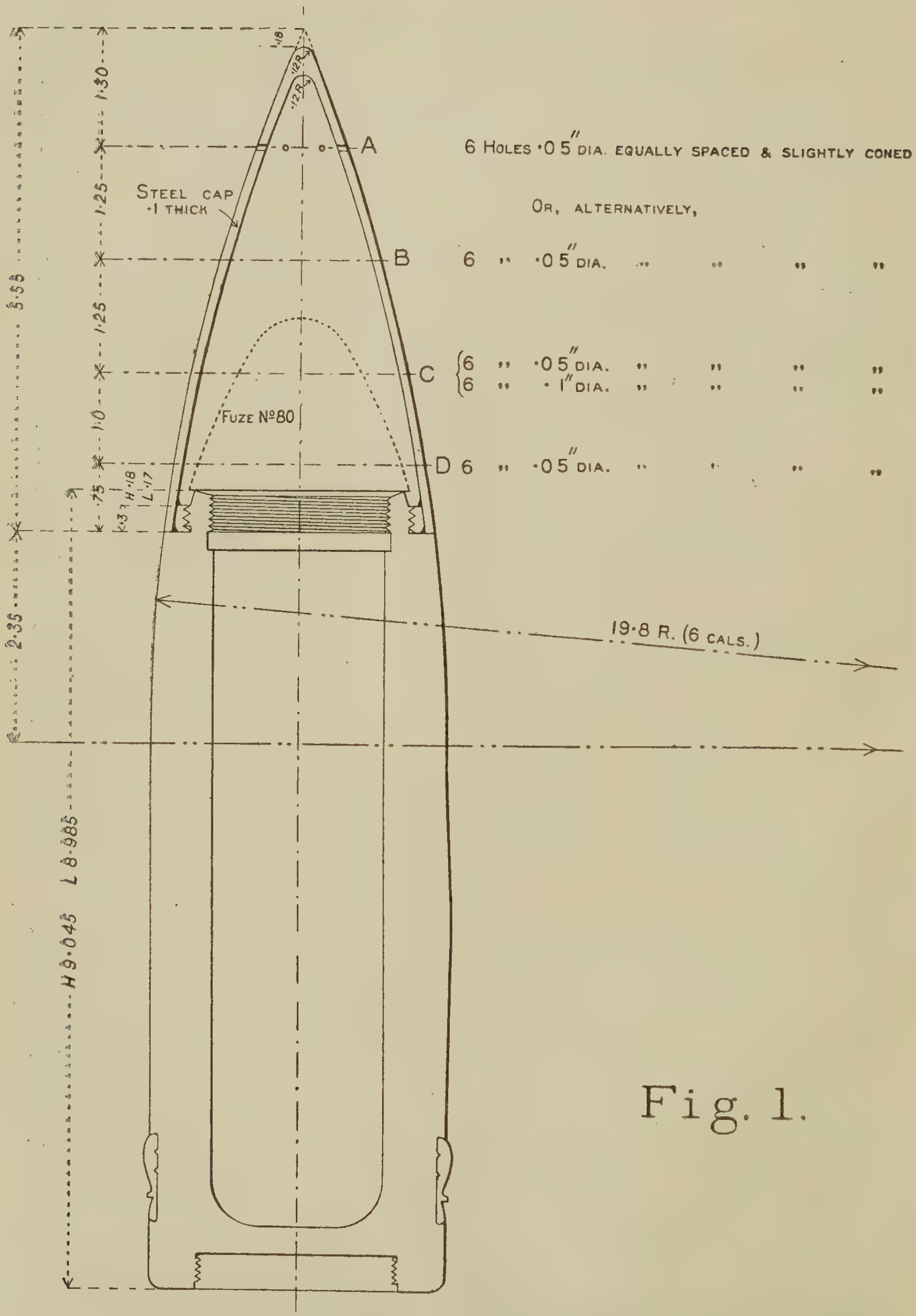
* In order to make use of these relations we must assume that *the total pressure on the outside of the (small) hole is the same as the total pressure at the same point of the shell in the absence of any hole.* This is the assumption made in all aerodynamical experiments on pressure distribution at low velocities. Its application to high velocities is at present incapable of justification, either experimental or theoretical. We shall return to this point in § 8.



5·55
1·30
1·25
1·25
1·0
·75
·18
·12R
·12R
A
B
C
D
Steel cap
·1 thick
Fuze No 80
H ·18
L ·17
·37
2·35
L 8·985
H 9·045
19·8 R. (6 cals.)
6 Holes ·05" dia. equally spaced & slightly coned
Or, alternatively,
6 " ·05" dia. " " " "
6 " ·05" dia. " " " "
6 " ·1" dia. " " " "
6 " ·05" dia. " " " "
Fig. 1.

Fig. 1.—18-pdr. capped shell, diameter 3·3 in., for pressure-distribution experiments, half size; dimensions quoted in inches.

total drag must be made up of the contributions of (1) the dynamic pressure on the head, (2) the (negative) dynamic pressure on the base, and (3) skin friction.

If we could simultaneously determine the total drag and the two contributions of the dynamic pressure over a range of velocities, we could probably make some advance to an understanding of the mechanism of the resistance of a compressible fluid at high velocities.

It seems probable, from general considerations, that the pressure on the exact nose of a shell will obey closely the formula given by Lord Rayleigh.* Caps with a hole at the nose precisely were not used in this trial; they could, however, be so used, and a direct test of Rayleigh's formula could be made, which would be of great interest. The curves shown in fig. 2 are of the same general shape as Rayleigh's curve for the point of the nose, but the pressure falls off so rapidly near the nose that a precise comparison on present results is not possible.

A number of difficulties, many of which will occur to the reader, have been tacitly ignored in the foregoing sections. These will be discussed later on in § 8.

§ 3. *Details of Firing Trials.*—An 18-pdr. field gun (on a high-angle mounting) was selected for the trial; the muzzle velocity, determined during the experiment, was 1603 f.s. The shells used are shown in fig. 1. The caps were rounded off at the apex, and the term "virtual point" will be used to denote the position of the point of a cap with a perfectly sharp point.

There were five series of caps, each with a ring of six holes. Four series had holes of diameter 0·05 inch and one series 0·1 inch; these series will be referred to by letters as follows:—

Table I.

Series letter.	Number of rounds.	Diameter of holes.	Distance of holes from virtual point of cap, measured along the axis of the shell.
		inches.	inches.
A	30	0·05	1·30
B	50	0·05	2·55
C	30	0·05	3·80
C*	30	0·1	3·80
D	30	0·05	4·80

Series C* was inserted as a control, to determine whether the effect of the size of the hole on the pressure was likely to be considerable.

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* "Aerial Plane Waves of Finite Amplitude," 'Scientific Papers,' vol. 5, p. 610.

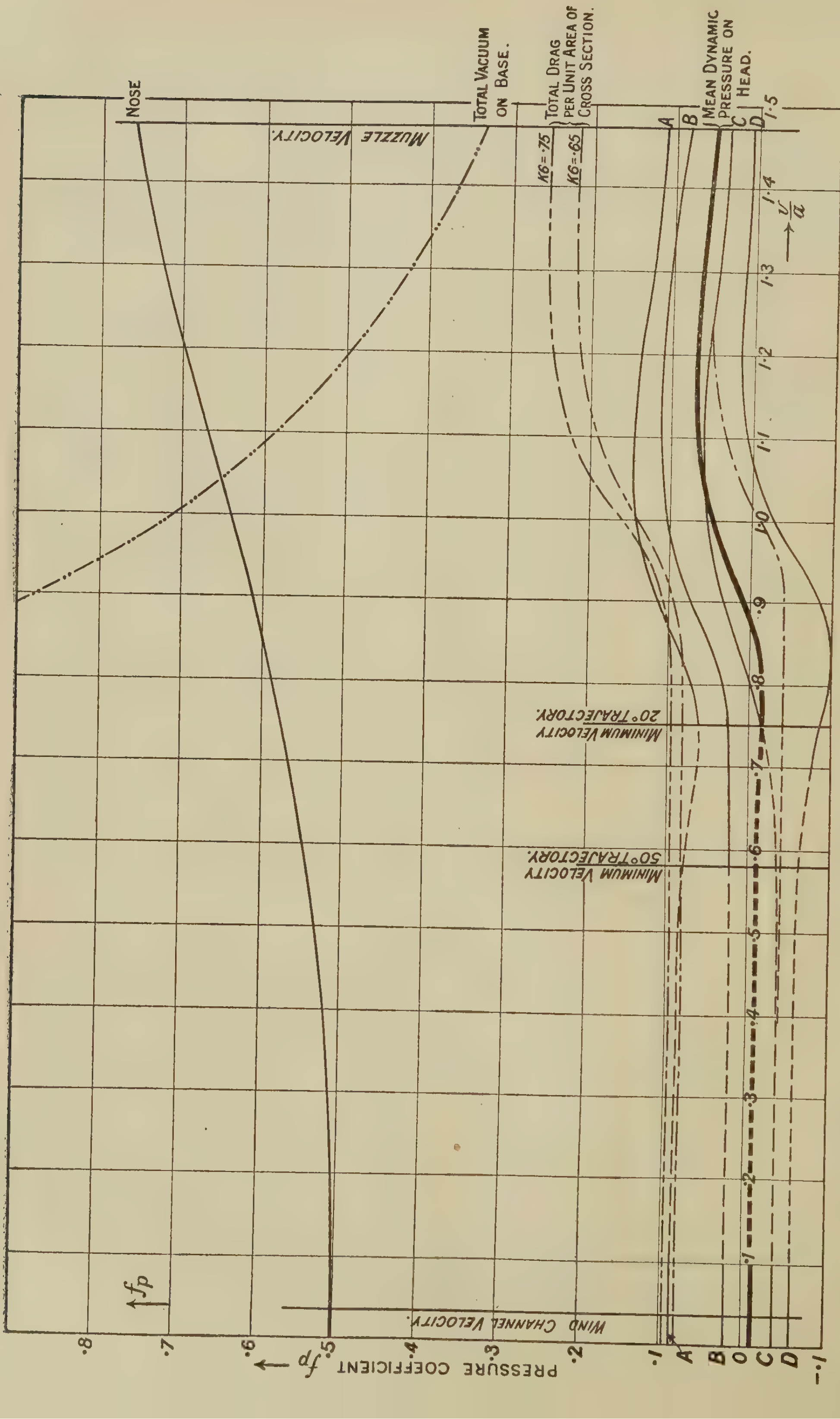
NOSE
TOTAL VACUUM ON BASE.
TOTAL DRAG PER UNIT AREA OF CROSS SECTION.
KG=·75
KG=·65
MEAN DYNAMIC PRESSURE ON HEAD.
A
B
C
D
MUZZLE VELOCITY.
MINIMUM VELOCITY 20° TRAJECTORY.
MINIMUM VELOCITY 50° TRAJECTORY.
WIND CHANNEL VELOCITY.
1·5
1·4
1·3
1·2
1·1
1·0
·9
·8
·7
·6
·5
·4
·3
·2
·1
v/a →
↑ fp
PRESSURE COEFFICIENT
← fp
·8
·7
·6
·5
·4
·3
·2
·1
A
B
0
C
D
−·1

Fig. 2.

EXPLANATION OF FIG. 2,

showing Curves of various Pressure Coefficients for the 18-pdr. Shell of fig. 1 as Functions of the Ratio of the Velocity of the Shell to the Velocity of Sound.

The pressure coefficient $f_p(v/a)$ is defined by $f_p(v/a) = \dfrac{\text{Dynamic Pressure}}{\rho v^2}$

where ρ is the density of the air,
v the velocity of the shell,
a the velocity of sound in the air,

and the dynamic pressure, ρ and v are measured in a self-consistent set of units.

The letters against the continuous curves refer to the series for which the curve in question represents the dynamic pressure.

The curve for the pressure coefficient at the nose is calculated by Lord Rayleigh's formulæ, quoted in § 6 (3).

The mean dynamic pressure coefficient over the head of the shell is shown by the thick curve continuous and dotted.

Ordinates are erected at the values of (v/a) corresponding to the muzzle velocity, and to the lowest velocities attained in the gun trials, and at the value corresponding to the wind channel experiments.

Between $(v/a) = 0{\cdot}1$ and the lowest velocity attained the curves are not determined, and are drawn — — — — — — —

The curve drawn — - — - — - — - — refers to the series C*, with larger holes ; the other four curves, drawn ——————— are strictly comparative.

The pressure coefficient for a complete vacuum on the base is shown by the curve drawn —— .. —— .. —— .. —— .. —— and the coefficient of total drag per unit area of cross-section by curves —— —— - - —— —— - - —— —— - - for two values of $\kappa\sigma$, namely, 0·65 and 0·75. The actual total drag coefficient lies between these curves.

Groups of five rounds were fired at fuze settings 3, 6, 9, 12, 16, 20 at an elevation of 20° in each series. The extra rounds in series B were fired at 50°. The majority of the rounds in series B were fired by day, and the position of the shell bursts was observed. The remaining rounds of all series were fired by night. Times of burning of the fuzes were recorded for all rounds fired; the means for each group are given in Table II.

Table II.—Mean Observed Time of Burning for each Group, and Average Residuals* of the Rounds in each Group, with the Recalculated Times of Burning. Times in seconds. Zero point taken as +0·24 fuze settings. (See § 4.)

Fuze setting.	Series A, 20°.			Series B, 20°.			Series B, 50°.		
	Recalculated.	Observed.	Average residual.	Recalculated.	Observed.	Average residual.	Recalculated.	Observed.	Average residual.
3	2·41	2·47	0·15	2·48	2·42	0·04			
6	5·15	5·28	0·08	5·02	5·34	0·12			
9	8·04	8·02	0·13	8·32	8·36	0·06	9·03	9·01	0·16
12	11·07	10·90	0·21	11·48	11·47	0·35	12·85	12·73	0·08
16	15·26	15·26	0·12	15·78	15·82	0·15	18·23	18·19	0·16
20	19·47	19·50	0·12	20·07	20·16	0·12	23·82	23·68	0·27
	Series C, 20°.			Series C*, 20°.			Series D, 50°.		
3	2·67	2·70	0·07	2·68	2·70	0·04	2·84	2·86	0·09
6	5·68	5·65	0·12	5·79	5·72	0·15	6·02	5·97	0·17
9	8·81	8·92	0·29	9·14	9·12	0·14	9·46	9·51	0·32
12	12·04	12·02	0·18	12·57	12·57	0·08	13·02	13·08	0·22
16	16·45	16·46	0·34	17·09	17·15	0·10	17·73	17·64	0·36
20	20·84	20·87	0·29	21·53	21·38	0·31	22·28	22·31	0·17

The following abnormal rounds are omitted from means and average residuals (see § 8):—

Series A: Set 20, 10·10; Set 16, 7·03; Set 12, 8·32.
Series B: 20°, Set 12, 5·7; Set 3, 1·92.
50°, Set 16, 16·89; Set 12, 8·03.
Series C: Set 12, 10·23; Set 9, 4·62, 7·81; Set 6, 3·98.
Series D: Set 6, 2·83; Set 3, 1·84.

The times were recorded to the nearest 0·01 second, but the time for any one round is not accurate to this degree. Experience has shown that under favourable conditions, such as obtained in this experiment, and with three or more observers, the time for any round can be determined with a probable error of 0·04 second.

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* The arithmetic average difference of the members of the group from the arithmetic mean of the group.

By means of the observations of position, the ballistics of the shells were determined. The conditions in the upper air were known from aeroplane observations. The wind structure was also observed. From these observations and routine calculations which need not be specified, the following quantities were determined and tabulated for the position of the shell at every integer second after gunfire along both the 20° and 50° trajectories :—

(1) The relative velocity of the shell and the air, v.
(2) The static pressure of the air, p.
(3) The density of the air, ρ.
(4) The ratio v/a, where a is the velocity of sound in the air.

§ 4. *Laboratory Determination of the Rate of Burning of the Fuzes.*—In order to determine the rate of burning of the fuzes used under the proper physical conditions, it is essential that laboratory experiments should be carried out with fuzes filled with the same batch of powder and under the same filling conditions as the fuzes used in the gun trials. Fuzes fulfilling these conditions may be described as *fuzes of the same lot.* The rate of burning of a fuze of given lot at given pressure and temperature varies largely with the spin, especially at low pressures. It is therefore essential to carry out the laboratory experiments with the fuze spinning at the correct rate, and (sometimes) at the correct temperature. As the *velocity* of the shell cannot affect the fuze, and the *deceleration* is small compared to the radial acceleration in the powder channels, the physical conditions of an actual firing trial are then properly represented in the laboratory experiment.

The initial spin of the shells in the trial was 11,660 revolutions per minute, and it may be assumed that it remains roughly constant for the fairly short times of flight with which we are concerned. In Table III the rates of burning of the fuzes used are given, determined at a spin of 11,750 revolutions per minute. This determination was effected by Mr. Goudie by coupling a dummy fuze body, holding the rings containing the powder train, to the shaft of a de Laval turbine; the dummy was run in an air-tight box with an automatic control of the pressure.

Experiments were also carried out to determine the effect of temperature and change of spin. Both these effects were negligible for the present trial.

The arbitrary graduations defining the fuze setting on these fuzes run from 0 to 22, and the length of powder burnt varies linearly with the fuze setting on this arbitrary scale. Consequently, under constant external conditions, the time of burning is a linear function of the graduations or fuze

Table III.—Showing the Relation between the Rate of Burning and the Pressure on the Vent Holes for the Fuzes used in this Experiment, determined by Mr. W. J. Goudie at University College, London.

Spin.—11,750 revolutions per minute.

The rate of burning is given in fuze settings per second. The pressure is given in atmospheres.

Rate of burning.	Pressure.	Difference.	Rate of burning.	Pressure.	Difference.
0·5	0·407	0·057	1·25	1·474	0·107
0·55	0·464	0·058	1·3	1·581	0·118
0·6	6·522	0·059	1·38	1·699	0·130
0·65	0·581	0·060	1·4	1·829	0·145
0·7	0·641	0·062	1·45	1·974	0·163
0·75	0·703	0·064	1·5	2·137	0·184
0·8	0·767	0·066	1 55	2·321	0·207
0·85	0·833	0·068	1·6	2·528	0·235
0·9	9·901	0·070	1·65	2·763	0·267
0·95	0·971	0·073	1·7	3·030	0·305
1·0	1·044	0·076	1·75	3·335	
1·05	1·120	0·080			
1·1	1·200	0·085			
1·15	1·285	0·091			
1·2	1·376	0·096			

setting except for very short times. The rates of burning of Table III are given in *fuze settings per second*, and apply to all stages of the combustion under constant external conditions. In order to construct from the observations, as accurately as possible, a curve of fuze setting against time of burning (see fig. 4, § 8), it is important to determine the constant in the above linear relation. This constant may be regarded as the fuze setting which burns for zero time and is called *the zero point* of the fuze. It is not necessarily at the zero graduation. Its position depends on the internal arrangement of the powder-train connections, and it must be determined by experiments on the actual fuze bodies used. It appears that the zero point of the fuzes used was +0·24 settings. It is assumed that this zero point remains unaltered when a fuze is fired from the gun. If this assumption is incorrect, the rates of burning observed during firing trials at short times will be in error, but those at later times will be unaffected.

§ 5. *Analysis of the Observations.*—The data provided by the observations described in §§ 3, 4, are sufficient, on analysis, to provide information as to the value of the dynamic pressure for values of v/a between 0·7 and 1·4* for each position of the holes in the cap. It is not necessary to describe in detail the numerical methods used. After the final results for the dynamic pressures were obtained, the inverse process was gone through of integrating the corresponding rates of burning to obtain the time for each fuze setting as a check on the accuracy of the work. These recalculated times are given in Table II, and it will be seen that the agreement with the observed time is satisfactory for all series, the difference between the two for any one group being less than half the average residual for the observed group in nearly all cases.

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* *Note added, March* 10.—Owing to the effect of an uncertainty in the zero point (see § 8), the values of the dynamic pressures for values of v/a greater than 1·2 must be given less weight than those for values of 1·2 and less.

In series B, which was fired at 20° and 50°, the recalculated times of burning are systematically slightly too short at 50° and too long at 20° at long settings. The differences, however, are not bigger than those for other series.

In the usual aerodynamical notation, the dynamic pressure may be put in the form

$$\rho v^2 f_p (v/a),$$

where v is the velocity, ρ is the air density, a is the velocity of sound, and f_p is a numerical coefficient known as *the pressure coefficient.* This coefficient f_p may (by the theory of dimensions) depend on other arguments besides v/a, but it is unlikely that any others are of serious importance in this connection. It is known that f_p is roughly constant at low velocities; this constancy probably persists nearly up to $v/a = 0{\cdot}7$. If pressure, density, and velocity are measured in any self-consistent set of units, f_p is independent of the set of units chosen, and is more suitable than the dynamic pressure itself for tabulation as it does not depend on ρ. The values of f_p, determined by these trials were calculated from the dynamic pressures, and are tabulated in Table IV as functions of v/a. They are also shown graphically in fig. 2.

Values of the pressure coefficients, determined in a wind channel at the National Physical Laboratory, at a velocity of 40 f.s., are also given in Table IV for the same positions of the holes along the axis of the shell. The dynamic pressures at this velocity were determined more exhaustively than this along the whole shell. It will be seen in Table IV or fig. 2, that the observed values of $f_p\,(0{\cdot}7)$ fit on satisfactorily to the wind channel values.

By plotting the values of f_p in Table IV for given values of v/a, opposite the position of the holes at which f_p was determined, a diagram is obtained, fig. 3, showing the distribution of dynamic pressure (coefficients) along the shell at high velocities. The curves are drawn for values of v/a equal to 1·47, 1·2, 1·0, 0·9, 0·75, and 0·04 (wind channel velocity). The values of the

Table IV.—Values of the Pressure Coefficient $f_p(v/a)$ as a Function of v/a for various positions on the Head of a Shell, as Determined by this Experiment, together with other Coëfficients of a similar nature.

v/a.	Values of $f_p(v/a)$.						$\bar{f}_p(v/a)$.	$f_B(v/a)$.	Total drag.	
	Point of nose.	Position of holes in cap of shell.					Contribution of dynamic pressure on the head to the drag per unit area.	Contribution of a total vacuum on base.	Total drag per unit area of cross section lies between these limits.	
		A.	B.	C.	C*.	D.				
	Calculated.	Determined by experiment.								
1·47	0·760	0·11	0·085	0·035	0·035	0·01	0·054	0·328	0·247	0·214
1·4	0·747	0·115	0·09	0·04	0·04	0·01	0·060	0·362	0·249	0·215
1·3	0·724	0·125	0·10	0·045	0·045	0·01	0·065	0·420	0·249	0·215
1·2	0·698	0·135	0·11	0·055	0·05	0·015	0·070	0·493	0·242	0·209
1·1	0·669	0·145	0·11	0·06	0·035	0·01	0·069	0·585	0·221	0·191
1·0	0·638	0·14	0·10	0·055	−0·01	−0·025	0·053	0·710	0·162	0·140
0·9	0·610	0·11	0·07	0·03	−0·04	−0·085	+0·010	0·876	0·106	0·091
0·8	0·585	0·07	0·03	0	−0·04	−0·095				
0·75	0·574	0·06	0·025	−0·015	−0·04	−0·085	−0·015	1·26	0·095	0·082
0·7	0·564	—	0·025							
0·6	0·546	—	0·025							
				Wind Channel Values.						
0·04	0·500	0·086	0·021	−0·039	−0·039	−0·061	−0·010	—	0·094	0·081

The values of $\bar{f}_p(v/a)$ obtained in this experiment are given to a nominal accuracy of 0·005. The values for the nose are calculated by Lord Rayleigh's formula (*loc. cit.*).

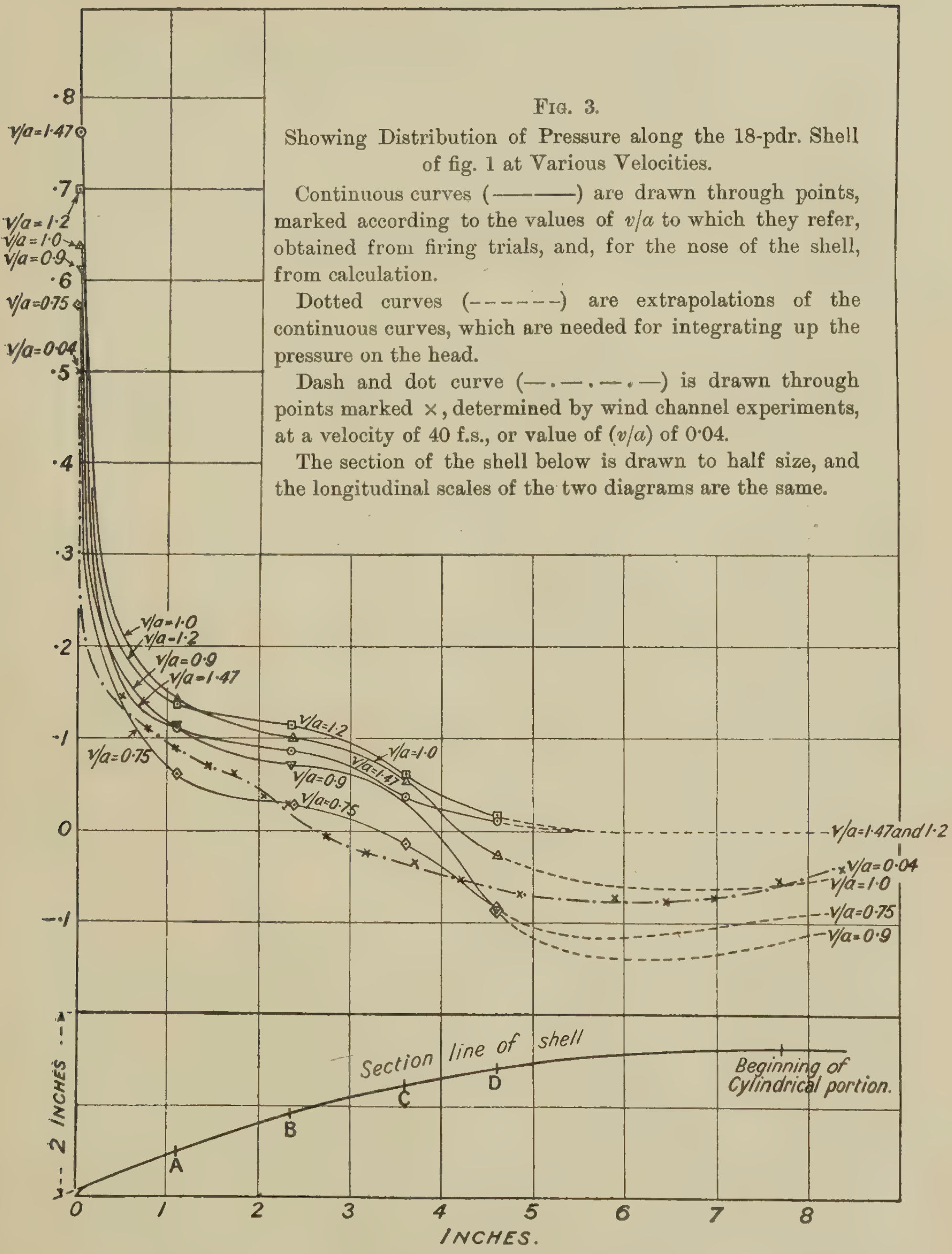

Fig. 3.

Showing Distribution of Pressure along the 18-pdr. Shell of fig. 1 at Various Velocities.

Continuous curves (————) are drawn through points, marked according to the values of v/a to which they refer, obtained from firing trials, and, for the nose of the shell, from calculation.

Dotted curves (– – – – – –) are extrapolations of the continuous curves, which are needed for integrating up the pressure on the head.

Dash and dot curve (—·—·—·—) is drawn through points marked ×, determined by wind channel experiments, at a velocity of 40 f.s., or value of (v/a) of 0·04.

The section of the shell below is drawn to half size, and the longitudinal scales of the two diagrams are the same.

pressure at the nose, at which these curves start, and the curve for the pressure at the nose, given in fig. 2, are calculated by Rayleigh's formulæ (*loc. cit.*).

In fig. 3 the exact shape of the curve between the nose and the position of the holes in series A is naturally not very definite. This is not important for the purpose of § 6, but it could be wished that the curves were determined by observation behind the position of the holes in series D.

§ 6. *Integration of the Pressure over the Head of the Shell.*—It can easily be shown that if $p(y)$ is the dynamic pressure at the point on the shell at which the distance from the axis is y, then the total force due to the dynamic pressure on the shell in its symmetrical position is along the axis and is given by the expression

$$2\pi\int_0^r y\,p(y)\,dy,$$

where r is the radius of the shell. The mean component of the dynamic pressure on the head, parallel to the axis of the shell, is therefore

$$\frac{2}{r^2}\int_0^r y\,p(y)\,dy,$$

and the coefficient of this contribution to the drag, or mean dynamic pressure coefficient $\bar{f}_p(v/a)$, satisfies the equation

$$\bar{f}_p\left(\frac{v}{a}\right) = \frac{2}{r^2}\int_0^r y f_p\left(\frac{v}{a}, y\right) dy. \tag{1}$$

This coefficient has been calculated for several values of v/a, and the results are given in Table IV and plotted in fig. 2.

Again, if we express the total drag R on the shell in the form

$$R = A\rho v^2 f_R(v/a), \tag{2}$$

where A is the area of the cross-section of the shell, then the drag per unit area is given by

$$R/A = \rho v^2 f_R(v/a).$$

The coefficient $f_R(v/a)$ is directly comparable to $f_p(v/a)$, the coefficient of the mean dynamic pressure over the head, which latter is one of its main contributors.

The values of f_R, the coefficient of the drag per unit area, are not known really accurately for shells of this shape. They certainly lie, however, between the two sets of numbers given in Table IV and the two curves of fig. 2, approximating to the lower values at high velocities and the higher values at low velocities.

The pressure coefficient $f_B(v/a)$, corresponding to a total vacuum over the base, is clearly given by the equation

$$f_B(v/a) = p/(\rho v^2) = \gamma^{-1}(v/a)^{-2}, \tag{3}$$

where γ is the ratio of the specific heats of the gas. Values of $f_B(v/a)$ are also tabulated in Table IV and plotted in fig. 2. It will be seen that the coefficient f_R is less at all velocities here reached than the coefficient f_B alone. The vacuum on the base is therefore by no means complete at a velocity represented by $v/a = 1{\cdot}5$.

It would be of very great interest if the precise degree of vacuum could be properly determined by experiment. This would not be possible by the use of a powder train fuze, for no such fuze will burn at all at the necessary low pressures.

§ 7. An immediate value attaches to the results now recorded, as they provide an adequate explanation of the complex behaviour of fuzes. The changes in rate of burning which accompany change of muzzle velocity or change of diameter of shell are all explained qualitatively by curves of the kind shown in fig. 2. It is now possible to predict the behaviour of fuzes before trial in a manner, and with a degree of certainty, unattainable prior to the war.

It is interesting to discuss briefly the records of pressure-distribution on the head of a shell in connection with other knowledge bearing on the point. The curves of fig. 2 show that at all speeds in the range covered the pressure has a maximum positive value at the nose of the shell. The pressure falls rapidly as the point of observation moves towards the base, and is negative some distance before the cylindrical part of the shell is reached. The determination of the pressure at the nose has only been made at low speeds ($v/a = 0{\cdot}04$), but is then found to be independent of the viscosity of the fluid medium. At these low velocities, calculations and experiments have shown that this independence of viscosity extends so far as sensibly to cover all positive dynamic pressures. The maximum observed pressure at the nose agrees with that calculated on the basis of an inviscid fluid, and the degradation of energy caused by viscosity shows an increasing effect as the point of observation recedes from the nose. The complete recovery of pressure on the base of a shell which is indicated by the theory of an inviscid fluid is not even approximately represented by the experimental value.

The reduction of the observations of the trial shoots has been made on the hypothesis that the effects of viscosity on the pressure on the head of a shell are negligible, and the results are quite consistent with that hypothesis. It may be expected, therefore, that the pressure could be calculated approximately from the equations of motion of a body in an inviscid compressible fluid. In the event of a solution of those equations, the observations now recorded would provide a suitable check on the soundness of the initial assumptions.

Viewed as an addition to the experimental investigation of the motion of shells, the trials have an importance which is too obvious to require detailed notice.

§ 8. *Possible Disturbing Factors, and Accuracy of the Results.*—In conclusion it may be well to return to a number of difficulties which have been more or less ignored in the earlier sections. We have stated that the pressure at the outside of the holes in the cap is practically the same as the pressure on the vent-holes of the fuze inside. The factors that might be thought to destroy this equality are (1) the centrifugal force in the rotating column of air between the vent-holes and the outside of the cap; (2) the pressure difference necessary to exhaust the products of combustion through the holes at the proper rate; (3) an initial delay while the interior of the cap is filling up to the true pressure outside. The effect of (1) is easy to calculate. In the case of (2) the maximum rate of efflux required is known from the composition of the powder and rate at which it is burnt. Observations were made of the pressure differences required to attain a measured rate of efflux with the actual caps. These observations also apply to (3). As a result it appears that the total pressure difference will only amount to more than 0·01 atmospheres for a very short time (of the order of 1/20 sec.) at the start. The effect is therefore completely negligible.

A far more serious question is, whether the pressure on the holes is actually the same as the pressure on the surface of the cap in the absence of the holes, the holes themselves being small. This is an accepted principle in aerodynamical work at low velocities,* and there seems no valid reason to expect it to fail at higher velocities. As a control of this assumption, the comparative series C and C* were fired; in C* the diameters of the holes were twice those of C. There is definite evidence that the dynamic pressures determined as above are different for these two series. The difference is not appreciable at the higher velocities, as the times of burning at setting (3) are the same, but for values of v/a between 1·1 and 0·8 the pressure determined by C* is distinctly less than the pressure determined by C (see fig. 2). The holes of the C* series are therefore not "small holes" at these velocities. It thus remains somewhat doubtful whether the holes of series A, B, C, D are really "small." If they are not, then the true dynamic pressures are probably somewhat higher. The difference is likely to be small, but it is not possible to assign to it a numerical upper limit.

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* The best direct experimental evidence will be found in the following papers: (1) G. Fuhrmann, "Theoretische und experimentelle Untersuchungen an Ballonmodellen," 'Jahrbuch der Motorluftschiff-Studiengesellschaft,' vol. 5, p. 12 (1911); (2) B. M. Jones and C. J. Paterson, "Investigation of the Distribution of Pressure over the Entire Surface of an Aerofoil," Advisory Committee for Aëronautics. Reports and Memoranda, No. 73, March, 1913.

The remaining points are less important. We have tacitly assumed that, throughout the motion, the axis of symmetry of the shell and the direction of motion of its centre of gravity coincide. The departures from this position of symmetry will be very small. They may exceed 1° or 2° initially for a short time, but for most of the motion they will be much less. The effect of such departures on the average pressure inside the cap has been determined at low velocities and is known to be very small indeed. The whole effect will probably be negligible here.

Finally, we come to the uncertainties in the behaviour of the fuze, and especially in the position of the zero point. All the fuzes used were subjected, as far as possible, to precisely similar treatment. There is no room for any suspicion of systematic differences between different parts of the material used. Random differences alone should remain, and the extent of these is shown by the average residuals of Table II. It will be observed also that a number of rounds are omitted from the means and mean differences of this Table. Since all these omitted rounds are *short*, and since they occur in all series except C* with its large holes, some occasional mechanical trouble, such as the blocking of the holes by slag or paint, is suggested.

On the other hand, an error in the zero point will cause systematic errors in all the dynamic pressures at the higher velocities. This is shown by fig. 4, where it is obvious that the precise position of Z will seriously affect the slope of the time-fuze setting curve for short times. It is by determining the slopes of such a curve that the rates of burning are obtained.

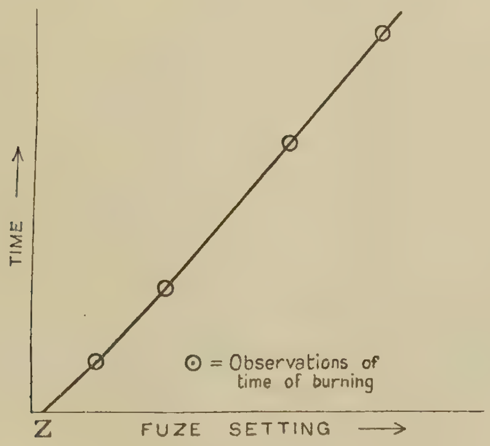

Fig. 4.

The final results have all been given to a nominal accuracy of 0·005 in f_p. This corresponds to an actual pressure of about 1/200 of an atmosphere at the velocity of sound. It must not be supposed that this represents the real accuracy of the results, especially at velocity ratios above 1·1 or 1·2, where the effect of the zero point may be serious. It does seem, however, possible to claim that the tables and curves of this paper give values of these coefficients of the true order of magnitude, and show correctly the type of change that takes place as the velocity of the shell passes through the velocity of sound.

An Experimental Determination of the Distribution of the Partial Correlation Coefficient in Samples of Thirty.

By Captain J. W. Bispham, R.E.

(Communicated by Prof. C. J Martin, F.R.S. Received November 26, 1919.)

Part I.—*Samples from an Uncorrelated Universe.*

1. *Introductory.*

In 1908[*] "Student" dealt experimentally with the distribution of the *total* correlation coefficient of small samples. In particular, he dealt with values of n as low as 4 for the case of zero correlation in the sampled population. In 1913 H. E. Soper[†] theoretically determined the mean correlation and the standard deviation of the distribution of correlations to second approximations. In 1915 R. A. Fisher[‡] gave an equation for the frequency distribution of r, and in 1917, as a result of a co-operative study by H. E. Soper, A. W. Young, B. M. Cave, A. Lee and K. Pearson,[§] this was reduced to suitable form for numerical manipulation, and the frequency distributions and frequency constants for samples of size ranging from $n = 3$ to $n = 400$ were given for values of the correlation in the sampled population ranging from $\rho = 0$ to $\rho = 0{\cdot}9$. The present experimental investigation was commenced in 1914, but had to be put aside during the war. It was intended to determine whether the distribution of partial correlation coefficients for samples as small as 30 showed greater dispersion than is observed for total correlation coefficients. Yule[||] has shown that for normal distributions and large samples the standard deviations of the distributions should be of the same magnitude. The experiment can now be related to the complete evaluation of the distributions of total correlations referred to above.*

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[*] 'Biometrika,' vol. 6, p. 302, *et seq.*

[†] 'Biometrika,' vol. 9, p. 91, *et seq.*

[‡] 'Biometrika,' vol. 10, p. 507, *et seq.*

[§] 'Biometrika,' vol. 11, p. 328, *et seq.*

[||] G. U. Yule, 'Roy. Soc. Proc.,' A, vol. 79 (1907).

2. *Nature of Sampled Population.*

The population to be sampled was obtained artificially as follows: Thirty "counters" bearing the numbers +1 to +15 and −1 to −15 were drawn in random order from a container and the numbers were written down in the order drawn. This set of thirty numbers represents the varying values of the first attribute. The values of the second attribute were obtained in exactly the same way, viz., the counters were returned to the container, shaken up, and drawn again in random order, the numbers drawn being written down beside the first set of thirty. Similarly, the varying values of the third attribute were obtained by a third draw. This artificial population has the advantage that the mean value of each attribute in each sample is zero, and further, the standard deviations are invariable from sample to sample. This saved a good deal of arithmetical work.

The frequency distribution of the attributes in the artificial population is very far from normal, being of rectangular form with a central strip missing, since any of the numbers except zero occurs as often as any other, while the number zero does not appear at all. A further advantage of so irregular a distribution lay in the fact that the investigation was intended, in part, to test the reliability of partial correlation coefficients obtained in respect of groups of registration districts used in a previous investigation, and in such cases the frequency distribution is, of course, irregular.

3. *Observed Distributions of Total and Partial Correlation Coefficients.*

The values of the total correlation coefficient between the various pairs of attributes will be referred to generally as r_{12}, r_{13}, and r_{23}. The partial correlation coefficient determined was that between attributes 1 and 2 for 3 constant. The notation ${}_3r_{12}$ will be used.

In all, 1000 cases were worked and the observed distributions are shown in detail in Table I.

The distribution given in column 6 is that deduced from the investigation referred to above. R. A. Fisher's† equation for the distribution is shown to lead to

$$y_{n+2} = \frac{2n-1}{n-1} \cdot \mathrm{K}_1 y_{n+1} + \frac{n-1}{n-2} \cdot \mathrm{K}_2 y_n,$$

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* 'Biometrika,' vol. 11, p. 328, *et seq.*

† 'Co-operative Study,' *loc. cit.*

where
$$K_1 = \frac{\rho r\sqrt{1-\rho_2}\sqrt{1-r^2}}{1-\rho^2 r^2}$$

and
$$K_2 = \frac{(1-\rho^2)(1-r^2)}{1-\rho^2 r^2}.$$

This is a very convenient form for the evaluation of the distributions for successive values of n.

Table I.—Total and Partial Correlation Coefficients: Frequency distribution for 1000 samples where $n = 30$ and $\rho = 0$ in each case.

(1) Range of r.	(2) Observed r_{12}.	(3) Observed r_{13}.	(4) Observed r_{23}.	(5) Observed ${}_3r_{12}$.	(6) Theoretical.†
+0·575 to +0·625	1	1			
+0·525 +0·575	1	2	2	2	1·7*
+0·475 +0·525	0	0	3	1	2·5
+0·425 +0·475	6	9	5	6	5·4
+0·375 +0·425	9	8	11	7	11·0
+0·325 +0·375	19	16	22	23	19·3
+0·275 +0·325	27	35	29	35	30·8
+0·225 +0·275	43	40	44	39	45·3
+0·175 +0·225	69	53	63	70	61·5
+0·125 +0·175	64	69	90	73	77·7
+0·075 +0·125	105	96	90	91	91·6
+0·025 +0·075	96	98	96	87	101·0
−0·025 to +0·025	112	120	104	118	104·3
−0·025 to −0·075	108	114	110	107	101·0
−0·075 −0·125	98	102	96	90	91·6
−0·125 −0 175	65	84	76	61	77·7
−0·175 −0·225	54	50	64	60	61·5
−0·225 −0·275	46	48	46	51	45·3
−0·275 −0·325	42	27	17	43	30·8
−0·325 −0·375	11	15	12	14	19·3
−0·375 −0·425	11	6	12	8	11·0
−0·425 −0·475	6	3	4	11	5·4
−0·475 −0·525	3	2	1	1	2·5
−0·525 −0·575	3	2	3	2	1·7*
−0·575 −0·625	0				
−0·625 −0·675	1				
Total	1000	1000	1000	1000	1000

* These are frequencies for the whole range to the limits of the distribution.

† 'Co-operative Study,' *loc. cit.*

In the paper in question the ordinates are given for $n = 25$ and $n = 50$. The ordinates for $n = 30$ were calculated by the method indicated above, and checked to six significant figures by the alternative method given on p. 332. The intermediate ordinates forming the beginnings and ends of the frequency groups were calculated by the latter method, and Simpson's formula was used for finding the areas, viz.,

$$\int_0^1 y\,dx = \frac{1}{6}\{y_0+4y_{\frac{1}{2}}+y_1\}.$$

An inspection of Table I leads one to expect a reasonably good fit in all cases. Before referring to the determination of "goodness of fit," it may be well to give particulars of the frequency constants of the observed distributions and of those calculated from the theoretical investigation.* These are given below :—

Table II.—Values of Frequency Constants of Distributions in Table I.

(1) Constant.	(2) r_{12}.	(3) r_{13}.	(4) r_{23}.	(5) ${}_3r_{12}$.	(6) Theoretical.
Mean	−0·0029	+0·0008	+0·0077	−0·0021	0·0000
μ_2	0·03396	0·03148	0·03287	0·03526	0·03448
σ_r	0·1843	0·1774	0·1813	0·1878	0·1857
μ_3	−0·000578	+0·000664	+0·000099	−0·000322	0·0000
μ_4	0·003455	0·003004	0·003152	0·003545	0·003346
β_1	0·00851	0·01413	0·00028	0·00236	0·00000
β_2	2·9948	3·0311	2·9158	2·85036	2·81362
$\frac{1-\rho^2}{\sqrt{n-1}}$	0·1857	0·1857	0·1857	0·1857	0·1857

On p. 371 of the paper in question, it is stated that the condition $\beta_1 = 0$. $\beta_2 = 3$ for Gaussian distribution is not attained for samples of 25 or 50. The distributions considered, however, are concerned with values of ρ as high as -9; and, for high values of ρ, the distributions of r are markedly skew. In the case now under consideration, however, the distribution is symmetrical, and an examination of Table II shows that the departure from the Gaussian type is not large. In fact, if the *theoretical* distribution be compared with the normal curve that fits it best—that is, the normal curve with the same standard deviation—it is found that, grouping the frequencies as below, the "goodness of fit," as measured by P, is $0{\cdot}98 \pm 0{\cdot}08$. This expresses in another way that, for the special case $\rho = 0$ and $n = 30$, the distribution of r's approaches closely to the normal, and, consequently, the standard deviation may be regarded as a good measure of the dispersion. The tabulated values of σ_r are subject to a probable error $\pm 0{\cdot}003$, and it may be noted that they do not depart significantly from the value obtained from the usual expression $\frac{1-\rho^2}{\sqrt{n-1}}$, which is itself identical to five places with the theoretical value.

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* 'Co-operative Study,' *loc. cit.*

4*a*. *Curve Fitting: Total Correlations.*

In the following Table III will be found the frequency distributions of Table I on 0·15 ranges centred about the tabulated value, together with the corresponding best fitting normal curve frequencies and the theoretical frequencies.

Table III refers to the three sets of 1000 total correlations. The frequency distributions of the best fitting normal curves to the observed distributions are referred to as follows:—

N_{12}—best fitting normal curve for r_{12}.
N_{13}—best fitting normal curve for r_{13}.
N_{23}—best fitting normal curve for r_{23}.
N_T—normal curve based on the theoretical value of σ_r as determined from the equations of the co-operative study.
T —theoretical distribution.

Table III.—Distribution of Total Correlation Coefficients.

Value of r.	(1) r_{12}.	(2) N_{12}.	(3) r_{13}.	(4) N_{13}.	(5) r_{23}.	(6) N_{23}.	(7) N_T.	(8) T.
+0·60, etc.	2	2·1	3	1·6	2	2·3	2·3	2·2
+0·45	15	19·0	17	15·9	19	19·2	19·4	18·5
+0·30	89	87·8	91	85·6	95	93·9	91·0	95·3
+0·15	238	228·0	218	234·7	243	239·9	230·3	230·8
0	316	316·1	332	327·6	310	320·9	313·8	306·4
−0·15	217	223·8	236	233·0	236	224·4	230·3	230·8
−0·30	99	92·5	90	84·4	75	78·7	91·0	95·3
−0·45	20	18·5	11	15·6	17	15·8	19·4	18·5
−0·60, etc.	4	2·1	2	1·6	3	2·3	2·3	2·2
Values of P	P = 0·77±0·29		P = 0·78±0·29		P = 0·988±0·06		P = 0·98	

Values of P are given at the foot of the columns as paired. Comparing the values of the actual distributions columns (1), (3) and (5) with the theoretical distribution given in column (8) we get for the various values of P.

r_{12} with T, $P = 0·83 \pm 0·27$,*
r_{13} with T, $P = 0·64 \pm 0·31$,
r_{23} with T, $P = 0·70 \pm 0.30$.

The value of P as between columns (7) and (8), *i.e.*, between the normal curve based on the theoretical value of σ_r and the actual theoretical distribution is as stated above $0·98 \pm 0·08$.

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* The probable error of P is rather large, as has been shown by Prof. K. Pearson, 'Phil. Mag.,' vol. 31, April, 1916.

4*b*. *Curve Fittings: Partial Correlations.*

The ensuing Table IV gives the corresponding frequencies of the *partial* correlations as observed, together with the corresponding values of, the best fitting normal curve to the distribution, the best fitting Pearson curve type 2 and the values of N_T and T as used above. In each case the values of P are given at the foot of the columns.

Table IV.—Frequency Distribution of Partial Correlation Coefficients.

Value of $_3r_{12}$.	(1) Observed distribution.	(2) $_3N_{12}$.	(3) Pearson curve, Type II.	(4) N_T.	(5) T.
+0·60, etc.	2	2·5	1·3	2·3	2·2
+0·45	14	19·8	19·8	19·4	18·5
+0·30	97	90·9	94·3	91·0	95·3
+0·15	234	227·4	228·4	230·3	230·8
0	312	310·4	305·6	313·8	306·4
−0·15	211	231·3	232·1	230·3	230·8
−0·30	108	94·1	97·5	91·0	95·3
−0·45	20	20·8	20·8	19·4	18·5
−0·60, etc.	2	2·7	1·3	2·3	2·2
Total	1000	1000	1000	1000	1000
		P=0·60±0·31	P=0·66±0·31	P=0·56±0·30	P=0·77±0·29

5. *Summary.*

It will be seen that the distribution of partial correlation coefficients is, on the whole, as well fitted by the theoretical distribution as are the distributions of total correlations. Comparing the four observed distributions with the distribution referred to as T, we have—

For distribution of r_{12}, $P = 0·83 \pm 0·27$,
For distribution of r_{13}, $P = 0·64 \pm 0·31$,
For distribution of r_{23}, $P = 0·70 \pm 0·30$,
For distribution of $_3r_{12}$, $P = 0·77 \pm 0·29$.

The P's all lie within the ranges of each other's probable errors so that it is not possible to say that one distribution is significantly better fitted than another.

The experiment indicates, *inter alia,* that values of the partial correlation coefficient (as determined by samples of 30) as great as $\pm 0{\cdot}5$ may be expected when the true value is zero, about 4 times per 1000, and further that the dispersion of partial correlation coefficients for $\rho = 0$ and $n = 30$ is not significantly different from that evaluated according to the co-operative study (*loc. cit.*) referred to above.

The results obtained above are of considerable practical importance. The partial correlation coefficient has been recently used in the analysis of many types of data. In the current psychological controversy* as to the existence of a central factor common to all forms of intellectual activity the method of partial correlation has been used in respect of groups of individuals of the size now under consideration. Considerable use has also been made of the partial correlation coefficient in analysing vital statistics and to refer to only one other sphere of application of the method a recent pamphlet† published by the Meteorological Office indicates the extent to which total and partial correlations have been used in analysing weather data.

A further experimental investigation is respect of samples from a highly correlated population has been in progress concurrently with the above and it is hoped to publish the results in due course as Part II of this investigation.

The numerical work in both cases has been extremely laborious.‡ In conclusion I beg to state that the investigation has been conducted under the general supervision formerly of Dr. E. C. Snow and latterly of Captain M. Greenwood and owes much to their help and advice.

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* Prof. Spearman, 'American Journal of Psychology,' vol. 15, p. 284; Cyril Burt, 'British Journal of Psychology,' vol. 3, pp. 94–177; W. Brown, "The Essentials of Mental Measurement," 'Camb. Univ. Press,' 1911; Dr. E. Webb, "Character and Intelligence," 'Brit. Jour. Psychology Monograph,' 1915; G. H. Thomson and J. C. M. Garnett, 'Brit. Jour. of Psychology,' vol. 9, p. 321, *et seq.*; J. C. Maxwell Garnett, 'Roy. Soc. Proc.,' Series A, vol. 96 (1919); Godfrey H. Thomson, 'Roy. Soc. Proc.,' Series A, vol. 95, 1918.

† M.O. 223, 'The Computer's Handbook,' sec. V, 3. A Collection of Correlation Coefficients from Meteorological Papers, and a Note on the Partial Correlation Coefficient. By Captain E. H. Chapman, R.E.

‡ I am especially indebted to Miss A. Fowler and to Mr. M. E. Wilson for help in this respect both for original working and for checking. Most of the original drawings were made by school children.

The Relation between the Refractivity and Density of Carbon Dioxide.

By P. Phillips, D.Sc.

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A number of different experimenters have determined the relation between the refractivity and density of various gases, and, with a fair agreement, they have come to the conclusion that the L. Lorenz and H. A. Lorentz formula $\left(\frac{\mu^2-1}{\mu^2+2} \cdot \frac{1}{\rho} = \text{constant}\right)$ is true within the limits of their experimental errors. At small densities this formula will, of course, reduce to either of the other two well-known relations, that of Drude ($\mu^2-1/\rho = \text{constant}$), or the empirical relation of Gladstone and Dale ($\mu-1/\rho = \text{constant}$). At greater densities the Lorenz and Lorentz formula is distinctly more accurate than the others, Drude's formula diverging the most rapidly. This is well brought out in an experiment by A. Occhialini, published in 'Il Nuovo Cimento,' August, 1914. Even the Lorenz and Lorentz formula is not accurately true, however, when applied to the large changes of density from a gas to a liquid. For example, for the green mercury line ($\lambda = 5461 \times 10^{-7}$) $\frac{\mu^2-1}{\mu^2+2} \cdot \frac{1}{\rho} = 0{\cdot}2065$ for water, while its value is 0·2082 for water vapour, a difference of 0·82 per cent.

It is thus evident that the densities used in the experiments with gases have not been great enough to exhibit the variations of the Lorenz and Lorentz constant. By experimenting with a gas just above its critical temperature large continuous changes of density may be produced and for this reason this experiment was carried out with carbon dioxide at a temperature of 34° C.

Nearer to the critical temperature than this the carbon dioxide is so sensitive to the smallest change in temperature or pressure that it was found too difficult to work with.

Continuous changes of density from 0·73 grm./cm.^{3} downwards were quite readily obtained, and by means of a Fabry and Perot étalon the continuous change in refractivity was observed.

General Arrangement of Apparatus.

The optical arrangement whereby the refractivity was measured is shown diagrammatically in vertical section in fig. 1. The light from a mercury lamp, M, was focussed by means of a condenser, C, on to the wide slit, S, of a collimator. After passing through the collimator it traversed a small Fabry and Perot étalon, E, was refracted through the prism, P, and then received by the telescope, T.

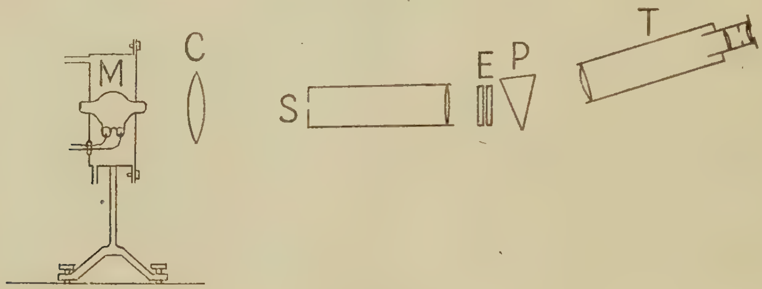

Fig. 1.

The étalon produced the usual circular systems of bands for the various wave-lengths existing in the light from the mercury lamp, but the slit, S, was adjusted so as to cut off all but a narrow horizontal strip across the centre of the systems. The prism, P, refracted the different wave-lengths by different amounts and so separated the strips of bands from one another in the telescope.

The Fabry and Perot étalon was placed inside a strong gunmetal chamber which is shown in section in fig. 2. The two plates of the étalon are shown

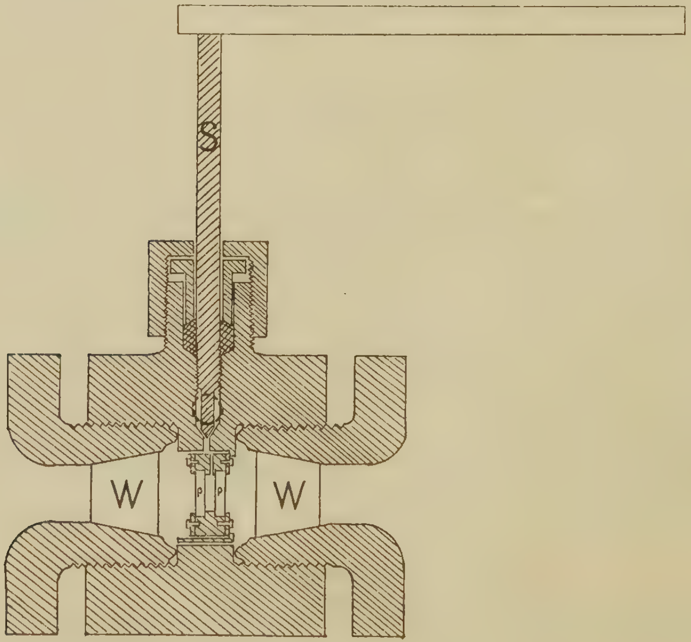

Fig. 2.

at P, P, and two thick glass windows at W, W. At S, is shown the stem of a pin valve which served to close the vessel or to allow it to communicate with the remainder of the apparatus through a tube which is indicated by the small dotted circle. The rest of the construction is perhaps made sufficiently clear by the figure. The internal capacity of the vessel when the étalon was in position was about 9 c.c. The methods by which this was measured are indicated later. The gunmetal chamber will be referred to as "the vessel" throughout this paper.

The vessel was immersed in vigorously stirred water contained in a copper tank which was provided with plate glass windows front and back. Considerable difficulty was experienced at first in maintaining the temperature of water sufficiently constant and a number of different forms of thermostat were tried. Ultimately a fine adjustment pin valve attached to a gas jet and operated by hand was found to be most satisfactory, and after a little practice one could keep the temperature constant to 0·01° C. for the whole of the day. After the vessel had been filled with the carbon dioxide it was placed into communication with a graduated glass cylinder of 250 c.c. capacity as indicated in fig. 3. This cylinder was placed in a water jacket and could communicate with the air through a tap, T, as well as with the vessel, V. The general construction is made clear by the diagram.

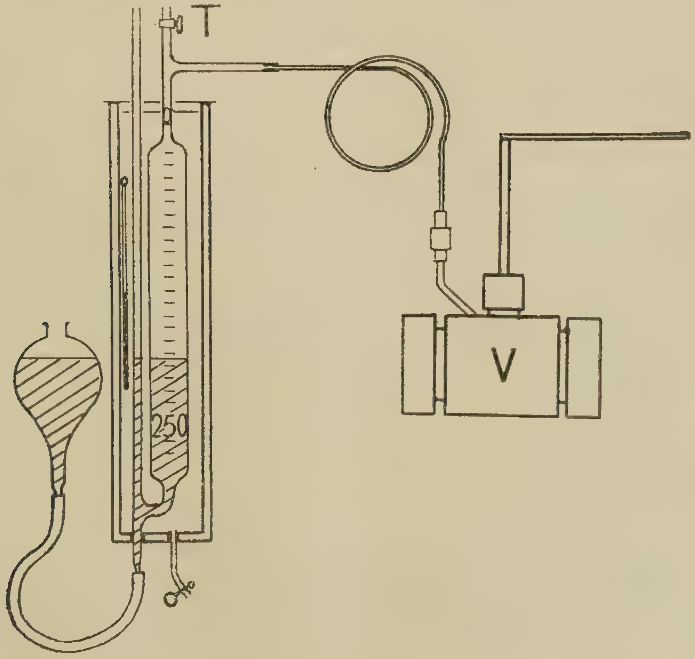

Fig. 3.

Method of Experiment.

The vessel was first evacuated and then connected with a cylinder of liquid carbon dioxide through a steel drying tube containing P_2O_5. It was then surrounded by melting ice placed in the copper tank. This caused the carbon dioxide to distil over into the vessel and completely fill it. The pin valve in the vessel was then closed, and the carbon dioxide cylinder shut off and disconnected.

A little of the carbon dioxide was then allowed to escape from the vessel until the latter was about three-quarters full. The vessel was then connected to the measuring cylinder as shown in fig. 3.

The ice was then removed from the tank and replaced by water which was heated to 34° C. and kept at that temperature for at least a quarter of an hour before any readings were taken. During this time the mercury lamp was started, the collimator and telescope were adjusted and the cross wire was placed on a particular green band ($\lambda = 5461 \times 10^{-8}$ cm.). The position of the cross wire on the other systems of bands ($\lambda\lambda = 4358, 5770, 5790 \times 10^{-8}$) was also estimated to one-tenth of a band. The mercury in the measuring cylinder was then raised to zero by raising the reservoir and opening the tap, T, fig. 3. This tap was then closed and the reservoir was lowered.

The pin valve in the vessel was then opened very slightly, thus allowing the carbon dioxide to escape very slowly into the measuring cylinder. While this was occurring the bands were slowly passing the cross wire and the number thus passing was counted for each of the systems of bands. Unless the escape was very slow the bands became indistinct and sometimes disappeared. This was obviously due to the carbon dioxide becoming heterogeneous when the expansion was too sudden. When about 25 green bands had passed the cross wire the pin valve was closed, thus stopping the escape of the carbon dioxide, and after the bands had become quite stationary the number which had passed the wire on each system of bands was estimated to one-tenth of a band. The volume of the carbon dioxide in the measuring cylinder was measured at atmospheric pressure and at the existing temperature of the water jacket. The tap, T, was opened, the reservoir of mercury again raised until the mercury in the graduated cylinder stood at the zero mark and the tap, T, again closed.

The process of allowing the carbon dioxide to escape into the measuring cylinder, counting the bands and measuring the escaped carbon dioxide was repeated until the gas in the vessel was reduced to atmospheric pressure. The vessel was then evacuated to about 1 mm. pressure and the number of bands counted during the evacuation.

Calculation of Results.

(*a*) *Density.*—The density at any particular reading of the bands was found by adding together all the volumes reduced to N.T.P. escaping into the measuring cylinder subsequent to the reading and adding to this the volume of the vessel reduced to N.T.P. from the existing atmospheric pressure and 34° C. Calling this total volume v, the volume of the vessel V, and the density of carbon dioxide at N.T.P. ρ_0, the density of the carbon dioxide in the vessel was $v\rho_0/\mathrm{V}$.

(*b*) *Refractive Index.*—Calling the distance between the Fabry and Perot plates d and the wave-length of the light used λ, the number of wave-lengths path difference at the centre of the ring system of bands is $2d/\lambda$.

If when the vessel is evacuated the cross wire is n bands from the centre, the path difference at the cross wire is $2d/\lambda-n$. Calling the total number of bands which pass the cross wire after the particular reading until the vessel is evacuated N, the refractive index is $\dfrac{\mathrm{N}+2d/\lambda-n}{2d/\lambda-n}$.

The calculation of the results requires the distance between the Fabry and Perot plates and the volume of the vessel.

The distance between the plates was obtained by measuring the brass spacing ring between them with a Browne and Sharpe screw gauge. This distance corrected to 34° C. was found to be $0{\cdot}1096\pm0{\cdot}0001$ cm.

The number of wave-lengths path difference to the centre of the band system for the green mercury line is, therefore, $2\times0{\cdot}1096/0{\cdot}00005461$, *i.e.*, 4014.

The measurement of the volume of the vessel was carried out in two ways.

(*a*) The vessel was completely filled with carbon dioxide at 0° C. and at the saturation pressure of the carbon dioxide in the cylinder. This was carried out as described in the method of experiment. The vessel was then connected to the measuring cylinder and the carbon dioxide in it was allowed to escape into the measuring cylinder in doses of about 200 to 250 c.c., the volume, temperature and pressure of each dose being measured just as is described in the method of experiment.

This was continued until the pressure in the vessel was reduced to atmospheric and then the volumes, reduced to N.T.P., were all added together.

Calling this total volume V, the density of carbon dioxide at 0°, and at the saturation pressure of the liquid carbon dioxide in the cylinder ρ_1, and the density of carbon dioxide at N.T.P. ρ_0, then the change of density in the vessel is $\rho_1-\rho_0$ and the volume of the vessel is $\mathrm{V}\rho_0/(\rho_1-\rho_0)$.

The following results were obtained on February 15, 1915 :—

Total volume reduced to N.T.P.	4470·2 c.c.
Temperature of carbon dioxide cylinder	7·3° C.
Saturation pressure (Amagat)	41·3 atmos.
Density of carbon dioxide at 0° C. and at 41·3 atmos.	0·9323 (Amagat)
Density of carbon dioxide at 0° C. and at 76 cm. when $g = 980{\cdot}62$	0·0019769
∴ at University College, London, where $g = 981{\cdot}19$	$\frac{0{\cdot}0019769 \times 981{\cdot}19}{980{\cdot}62}$

The volume of the vessel is therefore $\dfrac{4470{\cdot}2 \times 0{\cdot}0019769 \times 981{\cdot}19}{(0{\cdot}9323 - 0{\cdot}0020) \times 980{\cdot}62}$

$$= 9{\cdot}504 \text{ c.c.}$$

The mean of four determinations was **9·510** c.c.

(*b*) The second method of measuring the volume of the vessel was by carrying out the experiment as described in the method of experiment, but instead of filling the vessel with carbon dioxide it was filled with air at about 110 atmos. The air was deprived of moisture but not of carbon dioxide, and the value of the refractive index given by Cuthbertson* under the same conditions was assumed.

For the comparatively small changes of density which occur when using air it was found that the number of bands passing the cross wire was exactly proportional to the volume at N.T.P. of the air escaping into the measuring cylinder, and therefore within this range of density $(\mu - 1)/\rho$ is constant.

Using the same nomenclature as in the calculation of the refractive index of the carbon dioxide

$$\mu - 1 = \frac{\mathrm{N}}{2d/\lambda - n}, \qquad \rho = \frac{v\rho_0}{\mathrm{V}},$$

μ = refractive index of the air,
N = number of bands passing the cross wire,
d = distance between the plates of the étalon,
λ = wave-length of light used,
n = number of bands from the cross wire to the centre of the band system when the air was all pumped out,
ρ = density of the air,
ρ_0 = density of the air at 0° and 76 cm.
v = total volume of air at N.T.P. which escapes into the measuring cylinder,
V = volume of the vessel.

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* 'Roy. Soc. Proc.,' A, vol. 83 (1909).

For the green mercury line $\mu-1$ for air at N.T.P. = 0·0002936, and therefore

$$\frac{\mu-1}{\rho} = \frac{0{\cdot}0002936}{\rho_0}.$$

We, therefore, have

$$\frac{\mathrm{NV}}{(2d/\lambda-n)\,v\rho_0} = \frac{0{\cdot}0002936}{\rho_0},$$

and ∴

$$\mathrm{V} = \frac{0{\cdot}0002936\,v\,(2d/\lambda-n)}{\mathrm{N}}.$$

The following results were obtained on January 4, 1915:—

Total volume of air, reduced to N.T.P., escaping into measuring cylinder	990·8 c.c.
Total number of green bands passing the cross wire ...	122·6
Number of bands from cross wire to centre of band system at the close of the experiment	10
Temperature of vessel..	34·00 ° C.

Substituting these numbers in the equation we have

$$\mathrm{V} = \frac{0{\cdot}0002936 \times 990{\cdot}8 \times 4004}{122{\cdot}6} = 9{\cdot}5006 \text{ c.c.}$$

The mean of four determinations is 9·498 c.c. The other method gave 9·510 c.c., therefore the mean of both methods is 9·504 c.c., and that is the value used throughout the experiment.

A third method of measuring the volume was carried out. This was by filling the vessel with water and weighing it. The results were not very consistent with one another, however, probably owing to the difficulty experienced in completely filling and completely drying out the vessel. The mean result agreed quite closely with that given by the other two methods, but it was not used because it was obviously less reliable.

The two thermometers used were checked by comparing them with two mercury in Jena glass thermometers kindly lent by Mr. Eumorfopoulos, who had carefully calibrated them previously.

The measuring cylinder was calibrated by filling with mercury, running out the mercury to various divisions and weighing the mercury run out.

The barometer was 2 metres below the level of the apparatus, and therefore 0·02 cm. was subtracted from the corrected barometer reading.

Test for Expansion of the Vessel due to Internal Pressure.

It was suspected that this expansion of the vessel might be large enough to be appreciable and thus affect the calculation of the density.

To test this a capillary tube of 0·140 cm. internal diameter was fixed on to the tube leading from the vessel. The latter was completely filled with water, so that the surface of the water was near the top of the capillary tube, and then the top of the capillary tube was connected to a compressor.

The depression of the surface of the water for a given increase of pressure was observed, first, when the valve in the vessel was open, and, second, when it was closed. The difference gives the apparent contraction of the water in the vessel itself.

The results showed that the apparent contraction was the same as the contraction of the water itself, and therefore that the expansion of the vessel was inappreciable. As a contraction of 0·002 c.c. would be quite readily observed, and the volume of the vessel is over 9 c.c., the possible error due to the expansion cannot be more than 0·03 per cent.

The following figures were obtained in the test:—

Pressure.	Reading on capillary tube.			
	Valve open.	Difference.	Valve closed.	Difference.
atmos.	cm.	cm.	cm.	cm.
1	5·1	2·3	6·5	0·5
59	2·8		6·0	
1	5·5	2·3	6·5	0·5
57	3·2		6·0	
1	5·1	2·9	6·5	0·7
73	2·2		5·8	
1	5·2	2·85	6·5	0·7
71	2·35		5·8	

Therefore for the vessel alone we have:—

Pressure difference.	Depression in capillary tube.
atmos.	cm.
58	1·8
56	1·8
72	2·2
70	2·15
256	7·95

∴ 1 atmos. produces 0·03108 cm. depression.

Diameter of tube by mercury thread method .... 0·140 cm.
∴ apparent change in volume for one atmosphere ... 0·000479 c.c.
Volume of vessel.................................. .... 9·504 c.c.
Apparent compression per atmosphere .... $\left(\frac{0{\cdot}000479}{9{\cdot}504}\right)$

$$= 0{\cdot}0000503 \pm 0{\cdot}000002.$$

As the compressibility of water at 15° C. is 0·0000495, there is no difference between this and the apparent compressibility within the limits of the experimental error.

Test of Purity of the Carbon Dioxide.

It was originally intended to prepare the carbon dioxide carefully, so as to ensure its purity, but it was found that the carbon dioxide from the commercial cylinders, when introduced into the vessel in the way described, left a smaller residue when absorbed by caustic potash than that prepared by the experimenter. The carbon dioxide from the commercial cylinders was therefore used throughout the experiments.

In one test, 65 c.c., which was allowed to escape from the vessel, was collected over mercury at atmospheric pressure (74·9 cm.), and absorbed by 2 c.c. of strong KOH solution. The residue was measured at 8·7 cm. pressure, and was found to be 0·37 c.c. The volume at 74·9 cm. would therefore be $\frac{0{\cdot}37 \times 8{\cdot}7}{74{\cdot}9} = 0{\cdot}043$ c.c. This is 0·00066 of the total volume. This was the largest residue found, and therefore it is probable that not more than 0·1 per cent. of air was present.

Results of Determination of Refractivity.

The results obtained on February 3, 1915, are given as a sample, and after them are given the mean readings for six experiments carried out between January 20 and February 12.

Readings of February 3.

Corrected barometer reading.	Volume of CO_2 in measuring cylinder corrected to 0° and 76 cm.	Number of bands passing the cross wire.			
		Green (λ = 5461).	Yellow (λ = 5790).	Yellow (λ = 5770).	Violet (λ = 4358).
cm.	c.c.				
75·70	0	0·0	0·6	0·4	0·4
75·70	201·1	39·75	37·8	37·8	50·95
75·67	204·3	80·1	75·8	75·9	102·0
75·66	204·0	120·4	113·8	114·0	153·1
75·65	203·1	160·4	151·4	151·8	204·0
75·63	203·8	200·7	189·3	189·8	255·1
75·62	202·8	240·5	226·7	227·4	305·9
75·61	206·6	281·1	264·9	265·7	357·1
75·60	202·1	320·6	302·0	303·0	407·3
75·58	203·1	360·1	339·2	340·3	457·6
75·57	206·7	400·2	377·0	378·2	508·5
75·56	211·2	441·1	415·4	416·8	560·2
75·56	207·1	481·0	453·0	454·5	611·0
75·55	204·0	520·1	489·9	491·5	660·9
75·54	206·9	559·9	527·25	529·0	711·4
75·54	210·4	600·0	564·9	566·9	762·0
75·54	209·2	639·95	602·4	604·4	812·7
75·54	128·3	664·3	625·5	627·6	843·7
75·54	8·0	665·8	626·9	629·0	845·6

After this, one of the windows in the vessel cracked, and a new window was ground in, thus altering the volume of the vessel slightly. A further series of experiments was carried out in August and September, 1915, and these agreed very closely with those given below.

The temperature of the vessel was maintained at 34·00° C. throughout this and all the other experiments. At the close of the experiment the cross wire was 11·4 green bands, 10·7 yellow bands, and 14·5 violet bands from the centre of the band system. From these results we get:—

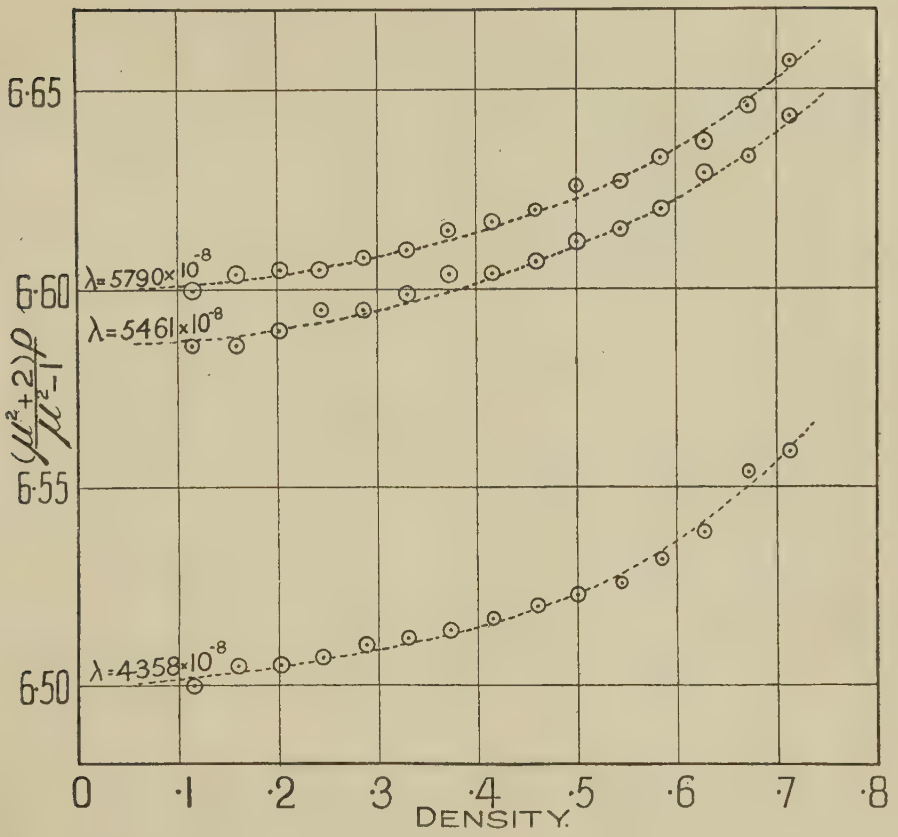
Path difference at zero density at the cross wire—

$= 4014-11 = 4003$ green wave-lengths ($\lambda = 5461 \times 10^{-8}$),
$= 3786-11 = 3775$ yellow wave-lengths ($\lambda = 5790 \times 10^{-8}$),
$= 5016-14 = 5016$ violet wave-lengths ($\lambda = 4358 \times 10^{-8}$).

Also we get:—

Total volume of CO_2 in the vessel reduced to 0° and to 76 cm.	Density ρ.	Refractivity $\mu-1$.			Inverse of the Lorenz and Lorentz constant $\frac{(\mu^2+2)\rho}{\mu^2-1}$.		
		$\lambda=5790$.	$\lambda=5461$.	$\lambda=4358$.	$\lambda=5790$.	$\lambda=5461$.	$\lambda=4358$.
3422·7	0·71235	0·1659	0·1663	0·1686	6·657	6·643	6·559
3221·6	0·67030	0·1561	0·1564	0·1584	6·646	6·633	6·554
3017·3	0·62777	0·1460	0·1462	0·1483	6·637	6·629	6·539
2813·3	0·58523	0·1359	0·1362	0·1380	6·633	6·620	6·532
2610·2	0·54300	0·1260	0·1262	0·1279	6·627	6·615	6·526
2406·4	0·50076	0·1161	0·1162	0·1178	6·626	6·612	6·523
2203·6	0·45853	0·1060	0·1062	0·1076	6·620	6·607	6·520
1997·0	0·41550	0·09590	0·09610	0·09728	6·617	6·604	6·517
1794·9	0·37356	0·08606	0·08623	0·08740	6·615	6·604	6·514
1591·8	0·33133	0·07623	0·07637	0·07731	6·610	6·599	6·512
1385·1	0·28820	0·06621	0·06635	0·06720	6·608	6·595	6·510
1173·9	0·24427	0·05602	0·05613	0·05692	6·605	6·595	6·507
966·8	0·20114	0·04606	0·04617	0·04677	6·605	6·590	6·505
762·8	0·15871	0·03629	0·03639	0·03681	6·604	6·586	6·505
555·9	0·11558	0·02645	0·02646	0·02687	6·600	6·586	6·499

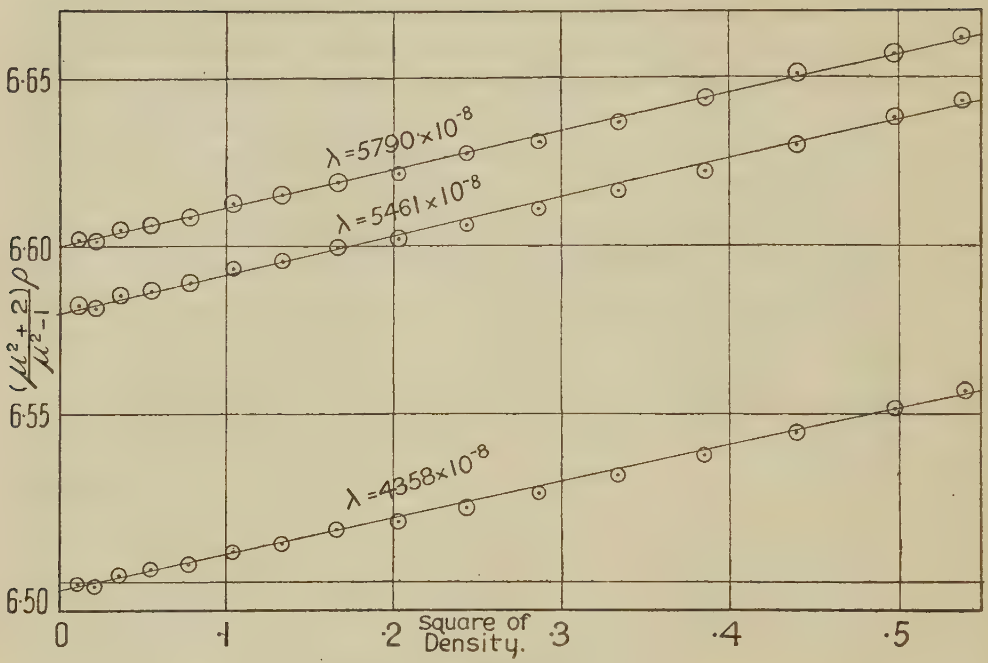
These results are plotted on Graph No. 1, which shows that $(\mu^2+2)\rho/(\mu^2-1)$ increases with ρ, but is not a linear function. The inverse of the Lorenz and Lorentz quantity is plotted for reasons which will appear in the discussion of the results. The mean results for six experiments are given below. In taking the mean, the densities which are most nearly equal in the six experiments are taken together and their mean taken. The mean of the refractivities corresponding to these densities is also taken.



GRAPH 1.

Density ρ.	ρ^2.	Refractivity $\mu-1$.			Inverse of the Lorenz and Lorentz constant $\frac{(\mu^2+2)\rho}{\mu^2-1}$.		
		λ = 5790.	λ = 5461.	λ = 4358.	λ = 5790.	λ = 5461.	λ = 4358.
0·73692	0·54305	0·17180	0·17238	0·17464	6·6620	6·6435	6·5580
0·70549	0·49772	0·16431	0·16479	0·16706	6·6571	6·6382	6·5518
0·66330	0·43997	0·15426	0·15477	0·15687	6·6515	6·6300	6·5445
0·62083	0·38543	0·14421	0·14470	0·14670	6·6440	6·6222	6·5380
0·57813	0·33423	0·13414	0·13456	0·13635	6·6368	6·6162	6·5322
0·53566	0·28693	0·12411	0·12450	0·12615	6·6315	6·6112	6·5271
0·49311	0·24315	0·11406	0·11444	0·11596	6·6280	6·6066	6·5222
0·45063	0·20307	0·10411	0·10422	0·10580	6·6218	6·6029	6·5182
0·40776	0·16627	0·09405	0·09433	0·095573	6·6192	6·5998	6·5158
0·36509	0·13329	0·08408	0·08433	0·085440	6·6155	6·5964	6·5115
0·32228	0·10386	0·07413	0·07432	0·075305	6·6129	6·5939	6·5090
0·27904	0·077861	0·064072	0·064262	0·065101	6·6090	6·5893	6·5056
0·23570	0·055555	0·054037	0·054195	0·054898	6·6067	6·5872	6·5040
0·19239	0·037014	0·044033	0·044162	0·044734	6·6050	6·5858	6·5022
0·14901	0·022203	0·034058	0·034162	0·034612	6·6020	6·5819	6·4988
0·10526	0·011080	0·024015	0·024088	0·024397	6·6023	6·5823	6·4991

These results are plotted in Graph No. 2.



GRAPH 2.

Accuracy of the Results.

The total number of green bands counted was about 650 for the greatest densities recorded, and about 100 for the smallest densities. As the bands can be estimated fairly reliably to one-tenth of a band the probable error in this part of the measurement is about 0·015 per cent. for the greatest densities and 0·1 per cent. for the smallest densities. The volumes can be estimated to one-tenth of a cubic centimetre, and, therefore, since they are measured in doses of a little more than 200 c.c., the probable error in this measurement is 0·05 per cent. The error in the measurement of the volume of the vessel and of the distance between the plates is probably about 0·1 per cent. The last two errors only affect the absolute values since they remain constant throughout.

Discussion of Results.

It is evident from Graph No. 2 that the inverse of the Lorenz and Lorentz constant is a linear function of ρ^2. For the wave-length 5461×10^{-8} the relation between the refractive index and the density is

$$\frac{(\mu^2+2)\rho}{\mu^2-1} = 6{\cdot}581\,(1+0{\cdot}0172\,\rho^2)$$
$$= 6{\cdot}581 + 0{\cdot}1130\,\rho^2.$$

Let us now consider the meaning of the term involving ρ^2.

Lorentz and Lorenz, in arriving at their constant, considered the effect produced on an electron of given free frequency by the alternating field in the light and by the field due to the polarisation of the surrounding molecules. The latter field was calculated by assuming the electron to be at the centre of a spherical cavity, the polarisation on the walls of which produced the field at the centre. This field, due to the polarisation, was calculated to be $4\pi P/3$, where P is the electric polarisation.

Lorenz and Lorentz have suggested that the field may not be exactly $4\pi P/3$, but may be $(4\pi/3+\sigma)P$, where σ is a small constant. This would lead to $(\mu^2+2)\rho/(\mu^2-1)$ being a linear function of ρ, which is not the case.

Natanson states that σ will depend upon the density of the medium. If we assume it to be directly proportional to the density, an equation is derived which is of the form obtained above from the experiment. The following calculation shows these results:—

Let m = mass of the electron of a certain type,
f = its restoring force per unit displacement,
ξ = its displacement,
n_0 = its free frequency constant = 2π/period,
t_0 = its period,
N = number of electrons of this type per cubic centimetre,
e = charge on one electron,
P = the electric polarisation = $N\xi e$.

For the free vibration we have

$$m\frac{d^2\xi}{dt^2} = -f\xi \quad \text{and} \quad n_0 = \sqrt{\frac{f}{m}}.$$

With an external field E and a field equal to $\left(\frac{4\pi}{3}+\sigma\right)P$, due to the polarisation of the medium, we have

$$m\frac{d^2\xi}{dt^2} = e\left[E+\left(\frac{4\pi}{3}+\sigma\right)P\right]-f\xi.$$

Put $$\xi = A\epsilon^{int}, \qquad E = B\epsilon^{int}.$$

Then $$(f-mn^2)\,\xi = e\left[E+\left(\frac{4\pi}{3}+\sigma\right)P\right]$$

or $$(f-mn^2)\frac{P}{Ne} = e\left[E+\frac{4\pi P}{3}+\sigma P\right]$$

$$E = P\left(\frac{f-mn^2-(4\pi/3)Ne^2-\sigma Ne^2}{Ne^2}\right).$$

Now $$\mu^2-1 = \frac{4\pi P}{E} = \frac{Ne^2}{(f-mn^2)/4\pi-Ne^2/3-\sigma Ne^2/4\pi}.$$

Put $$f-mn^2/4\pi = a.$$

$$(\mu^2-1)a-(\mu^2-1)(\tfrac{1}{3}-\sigma/4\pi)\mathrm{N}e^2 = \mathrm{N}e^2,$$

$$(\mu^2-1)a = \mathrm{N}e^2\left(1+\frac{\mu^2-1}{3}+\frac{(\mu^2-1)}{4\pi}\sigma\right)$$

$$= \mathrm{N}e^2\left(\frac{\mu^2+2}{3}+\frac{(\mu^2-1)}{4\pi}\sigma\right)$$

∴ $$\frac{(\mu^2+2)}{\mu^2-1}\mathrm{N}e^2 = 3a-\frac{3\sigma}{4\pi}\mathrm{N}e^2.$$

Putting $\mathrm{N}e^2 = k\rho$, ρ being the density,

$$\frac{(\mu^2+2)\rho}{\mu^2-1} = \frac{3a}{k}-\frac{3\sigma\rho}{4\pi}.$$

If σ were a constant, as suggested by H. A. Lorentz, then $\frac{(\mu^2+2)\rho}{\mu^2-1}$ would be a linear function of the density, whereas if, as suggested by Natanson, it is a function of the density, we may assume it to be directly proportional to the density, and so make $\frac{(\mu^2+2)\rho}{\mu^2-1}$ a linear function of the square of the density.

Comparing the last equation with the one derived from the experiment, we have for the wave-length 5461×10^{-8} in carbon dioxide

$$-\frac{3\sigma\rho}{4\pi} = 0{\cdot}1130\rho^2.$$

This gives $$\sigma = -0{\cdot}473\rho,$$

and the field at any point due to the polarisation

$$= \left(\frac{4\pi}{3}-0{\cdot}473\rho\right)\mathrm{P}.$$

For wave-length $\lambda = 5790$, $\sigma = -0{\cdot}477\rho$,

and for $\lambda = 4358$, $\sigma = -0{\cdot}460\rho$.

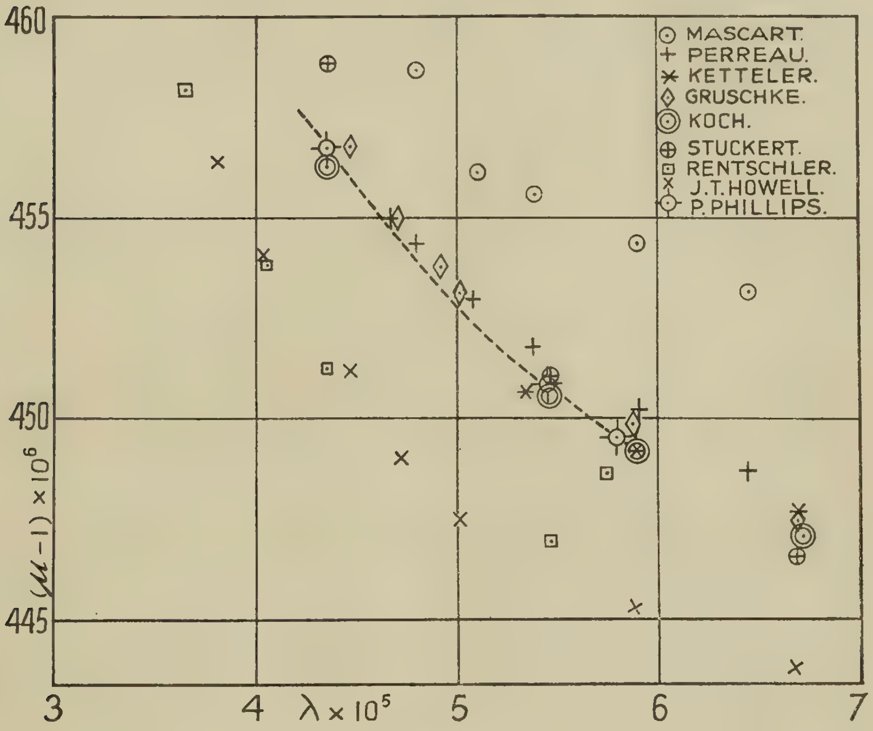
Comparison with previous Results.

It will be seen from Graph No. 2 that the values of $\frac{(\mu^2+2)\rho}{\mu^2-1}$, when the density is 0·0019780, *i.e.*, the density at 0° C. and at 76 cm., are as follows:—

λ.	$\frac{(\mu^2+2)\rho}{\mu^2-1}$.	$(\mu-1)\times 10^7$.
5790	6·6005	4495·4
5461	6·5810	4508·8
4358	6·4975	4566·8

This gives a dispersive power between $\lambda = 5790$ and $\lambda = 4358$ of 0·0158.

These values for $\mu-1$ are plotted on Graph No. 3, together with the values for different wave-lengths given by Mascart, Perreau, Ketteler, Gruschke, Koch, Stuckert, Rentschler, and J. T. Howell.



GRAPH 3

At density 0·7 grm./cm.^{3} the following values of $(\mu^2+2)\rho/(\mu^2-1)$ are obtained from Graph No. 2, and the values of $\mu-1$ are calculated from them :—

$\lambda\times10^7$.	$\frac{(\mu^2+2)\,\rho}{\mu^2-1}$.	$\mu-1$.
5790	6·6558	0·16313
5461	6·6362	0·16351
4358	6·5500	0·16574

The dispersive power between $\lambda = 5790\times10^{-7}$ and $\lambda = 4358\times10^{-7}$ is found from these numbers to be 0·0159, which is the same as that at the lower density within the limits of the error of the experiment.

In conclusion, I wish to thank Dr. A. W. Porter, of University College, London, for his kindly interest and helpful suggestions throughout the experiment. I also wish to acknowledge that some of the expense of the experiment was met by a Government grant.

As is stated above, this experiment was completed in 1915. A sojourn in the army has, however, prevented its earlier preparation for publication.

On the Viscosities and Compressibilities of Liquids at High Pressures.

By J. H. Hyde, A.M.Inst.C.E., A.M.I.Mech.E.

(Communicated by Dr. J. E. Petavel, F.R.S.—Received December 19, 1919.)

(From the National Physical Laboratory.)

The research here described was undertaken for the Committee on Lubricants and Lubrication of the Department of Scientific and Industrial Research, for the purpose of the analysis of the results of a previous investigation into the efficiency of power transmission through a worm gear when different kinds of oil, animal, vegetable, and mineral, were used as the lubricant. Since pressures of the order of 5 tons per square inch between the lubricated surfaces of worm gears are not uncommon, a knowledge of the rates of variation of the viscosities of the oils up to these pressures was essential, and as this information was not obtainable, the experiments necessary for the determinations were put in hand at the request of the Committee.

On looking into the question of suitable experimental methods, a direct measure of the changes of viscosity of the oils under pressure did not seem promising, and, therefore, the work was divided into two stages. In the first place, experiments were undertaken in which the values of the kinematical viscosity (η/ρ) was determined, and after this investigation was completed, apparatus was devised for the study of the changes of density with pressure.

The possibility of the existence of a considerable variation in the values of the viscosities between the ordinary pressures at which they are usually obtained in viscometers and pressures of the order of 5 tons per square inch appeared to be probable from the results obtained by Prof. O. Faust at Göttingen in 1914 for the cases of ethyl-ether, ethyl alcohol, and carbon bisulphide.

PART I.—*Apparatus for the Determination of the Absolute Kinematical Viscosities of Liquids at High Pressures and the Results obtained from it in the case of certain Lubricating Oils.*

For this research, a novel method was suggested by Dr. T. E. Stanton, which, in his opinion, possessed advantages over that previously used by Faust from the point of view of accuracy and simplicity.

The apparatus required in this method consists essentially of a system of two horizontal tubes (the upper one of capillary dimensions) and two vertical tubes, forming a closed circuit of liquid under pressure, the lower half of the circuit containing mercury and the upper half the liquid under test. One end of the tubular frame rests on a horizontal knife-edge, and the frame is supported in a horizontal position by a spiral spring. On the mercury being displaced by a given amount, flow will take place round the circuit, owing to the difference of head, and it is evident that, if the spring be so designed that its rate of extension is equal to the rate of change of head of the mercury, flow of the liquid under test will take place through the capillary tube under a constant pressure difference and, at a velocity which can be calculated from the rate of extension of the spring. In this way all the data required for the determination of the absolute kinematic viscosity of the fluid are determined.

After some preliminary experiments, this method was adopted and the design of the complete apparatus and the carrying out of the experiments was undertaken by the author.

A simple glass apparatus was first constructed to gain familiarity with the method and to obtain information on which to design the high pressure instrument. A diagrammatic sketch of the glass apparatus is given in fig. 1.

The instrument consists of a **U**-tube, the limbs A and B of which are connected together at their lower ends by a large-bore tube and at their upper ends by a capillary tube C, as shown. The whole is mounted on a frame supported by a knife-edge D, and so arranged that the left-hand side is heavier than the right.

The lower half of the circuit is filled with mercury and the upper half with the liquid under experiment. The motion of the frame is governed by the extension of a spring S, to which it is connected through the supporting arm F, terminating in a pointer which moves over a finely divided scale.

The method of experiment is as follows:—

The tilting frame is set in such a position that the horizontal tubes are truly level and the scale is adjusted so that the pointer reads zero. A tilt is given to the frame by moving the pointer vertically upwards, the taps T and

P being open. The tilt causes a flow in the U-tube, and when this flow has ceased the taps are closed and the frame is restored to its original position,

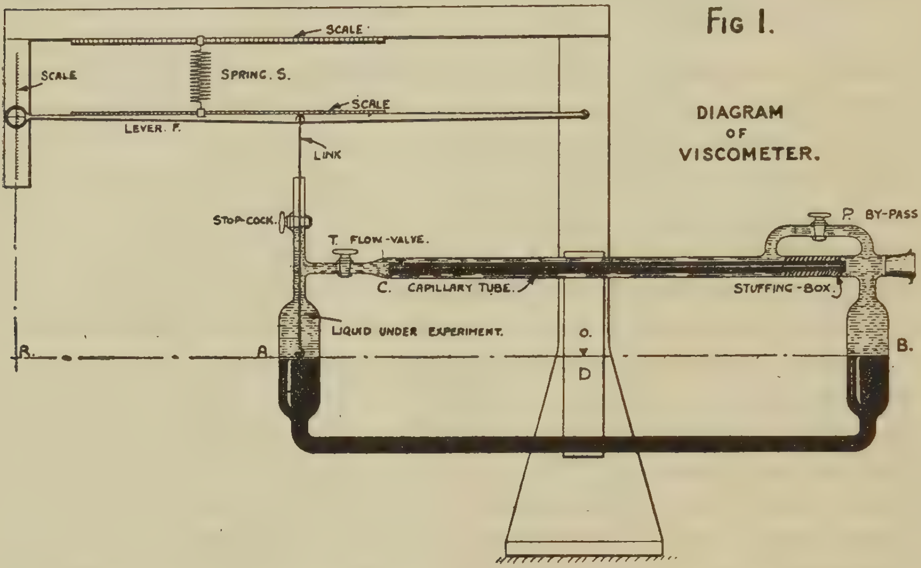


FIG I.

DIAGRAM OF VISCOMETER.

with the pointer at zero, the tension of the spring being adjusted to support the frame in this position. The head of mercury now in the U-tube can be calculated from the motion which has been given to the pointer and from the distances OR and AB.

If now the tap T is opened, the liquid will flow through the capillary tube from A to B, and the mercury from tube B to tube A. It is arranged that the stiffness of the spring is such that the tilt of the frame, due to the extra weight of mercury, exactly compensates for the loss of head which would have occurred if no tilt of the frame had taken place. The effective stiffness of the spring is adjusted by altering its position along the lever F. By the use of the spring in this manner a constant head of mercury is obtained, and also, the fall of the frame as indicated by the pointer gives a measure of the volume of liquid which has passed from one side to the other.

For example, suppose $OA = OB = AR$ (measuring to the axes of the vertical tubes), then the head of mercury is given directly by the scale, and the volume of liquid which has passed from A to B is obtained from the product of half the drop of the pointer during the measured time, and the area of the cross-section of the tube A or B (these being equal in diameter).

After the head and spring have been accurately set, the head remains constant throughout, and all that is required for the calculation of the viscosity is the rate of fall of the pointer over the scale.

The coefficient of viscosity is obtained by substituting the values of time and volume in the equation :—

$$\eta = \frac{\pi \rho g h r^4 t}{8 v l}$$

where η = coefficient of viscosity, ρ = density of liquid, h = head of liquid (calculated from known head of mercury in liquid), g = acceleration of gravity, r = radius of capillary tube, t = time, v = volume, l = length of capillary tube.

The High Pressure Apparatus.

Viscometer.—The parts of the apparatus which were subjected to the pressure were made of high tensile steel. The vertical tubes corresponding to A and B of fig. 1 were 1·5 cm. bore, ground and lapped truly parallel and cylindrical, and 4 cm. outside diameter. Full-bore plugs were provided at the lower ends of these tubes for cleaning purposes. The lower horizontal tube was of hydraulic tubing, polished inside. Holes, suitably plugged, were provided so that this tube could be cleaned mechanically.

The upper ends of the two vertical tubes terminated in valve boxes connected together by the upper horizontal tube. The latter was of hydraulic tubing, polished internally and about 1 cm. bore. The right-hand valve box carried the stuffing-box and glands for the glass capillary tube, and the by-pass for the latter with the valve P. The left-hand valve box contained the valve T for controlling the flow of the liquid in the apparatus and also the valve or stopcock on the pipe from the pressure supply.

The latter valve and also the by-pass valve P took the form of small truncated cones, with a small hole in the side of the conical portion leading to a central hole. The former hole corresponded with a hole of similar size in the valve box, and consequently a small rotation of the valve served to shut it.

It was arranged that the large end of the cone was inside the apparatus, so that the pressure forced the valve on its seat rendering packing unnecessary. The two valves were carefully ground in and gave little trouble, except with liquids which were not lubricants. They were provided with square heads and operating keys.

The valve T was a plain cylindrical rotary valve with a hole in its side leading from the hole in the top of the tube A to a central hole in the valve, and thence to the upper horizontal tube. The valve was packed with leather and the whole was made in such a manner that it could be manipulated with moderate ease from above the surface of the oil in the bath in which the apparatus was immersed during an experiment.

The stuffing-box for the capillary tube was packed with leather, and was so designed that the area of packing exposed to the pressure at one end was in excess of that at the opposite end, in order that the pressure should be utilised to keep the packing tightly squeezed. The gland was screwed home as tightly as possible, but, after high pressure had been applied, it was always possible to screw it further, showing that the desired effect had been obtained. The glass tube was considerably roughened where it passed through the leather packing.

The right-hand valve box was provided with a large hole on the right side for the admission of the capillary and for cleaning purposes. This hole was closed with a screwed plug fitted with a thermocouple, which is described later

Knife-edges and Plates.—The horizontal tubes of the viscometer were spanned at the centre of their length by an aluminium frame which carried the steel knife-edges.

A steel frame supported the viscometer from the bottom of the bath, and a bridge across this frame held the agate knife-edge plates. This frame also carried a device by which the viscometer could be tilted by a fixed amount and clamped in this position for the operation of the valves. An arrester, somewhat on the lines of that of a chemical balance, was also fitted, by which the viscometer could be lifted very slightly off its knife-edges and clamped in a horizontal position.

The pointer was fixed at the end of a horizontal lever pivoted at the centre of the supporting frame vertically above the main knife-edge, and connected by means of a vertical link to the viscometer tube A. The link was attached to the latter tube in the same horizontal line as the main knife-edge, the system forming a parallel motion. All connections were made by small knife-edges.

The lever was provided with a small scale along its length corresponding to a similar scale on a horizontal beam above, supported from the main frame. The spring was attached to sliding carriages on these two scales, so that the position of its ends from the centre of the system could be set accurately to any desired value.

The pointer took the form of a hair-line cross wire, and its passage over the vertical scale was observed by means of a telescope some 5 feet distant.

Thermocouple.—The thermocouple was provided to ensure that the temperature inside the apparatus was equal to that recorded by the bath thermometer, and to give, also, an indication of the time required to attain any particular temperature. Two thermocouples, one inside the apparatus and one in the bath, were opposed in a galvanometer circuit, and the galvanometer thus indicated any difference in temperature between the liquid in the viscometer and the liquid in the bath.

Oil Bath.—The bath in which the apparatus was immersed consisted of a rectangular tank, with semicircular ends, supported in a wooden box. There was a space of 2 inches between the box and the tank on all sides, and this space was filled with granulated cork lagging. The bath was fitted with a thermosyphon arrangement, and the heat supply was regulated by a toluene-mercury thermostat.

Stirrer.—The stirrer consisted of six small propeller blades attached to a horizontal shaft near the bottom of the bath. The shaft was driven through bevel gearing and a vertical shaft by a small electric motor. Lagged covers were supplied for the top of the bath.

It was possible to regulate the temperature of the bath oil to about 0·1° C., and this was left at the desired temperature for some hours, usually overnight, before experiments were made, to ensure that the temperature of the liquid inside the viscometer was the same as that of the bath.

Capillary Tubes.—All the tubes selected were measured for outside diameter at several positions along their lengths and in two directions at right angles. Tubes that did not show a tolerably uniform and circular section on the exterior were rejected as being unlikely to give satisfaction on the internal diameter. After cleaning and drying the selected tubes, each bore was accurately calibrated by measuring the length of a thread of mercury of determined mass, at various positions in the bore. In all cases accurate correction was made for the volume occupied by the mercury meniscus.

The following are the numerical results of the calibration :—

Table I.

	Tube No. 1.	Tube No. 4.	Tube No. 5.	Tube No. 7.
Average internal diameter (d) of tube corresponding to position (a)	0·03950	0·10192	0·13354	0·17706
Ditto (b)	0·03962	0·10200	0·13350	0·17757
Ditto (c)	0·03986	0·10216	0·13450	0·17785
Average value of $d^4 \times 10^6$ (mean value of d^4 for each position, (a), (b) and (c))	2·493	108·35	320·9	992·5

The individual values of the bores, as determined above, are accurate to within one part in four thousand. The accuracy of the above values of d^4 depends on the extent of the irregularities of the walls. Calibrations were not attempted with a short mercury thread measured in a large number of positions along the bore of a tube.

Preliminary Tests of Apparatus, Valves, etc.—A glass rod was substituted for the capillary tube to test for leakage in the valves T and P and through the stuffing-box. It was found that under the maximum mercury head available in the apparatus there was no leakage whatever during the course of two hours. This test was repeated at a pressure of 8 tons per sq. in. and no leakage either past the valves or past the glass rod was observed.

"*Head.*"—Arrangements were made to substitute a chemical balance for the spring, and connection was made to the spring lever vertically over the point of attachment of the link connecting the lever with the viscometer. Knife-edges were used throughout. By means of the balance, the extra weight of mercury (less the weight of an equal volume of liquid) passing over to one side due to a definite tilt of the apparatus could be obtained.

The various leverages and the diameters of the vertical tubes or cylinders being accurately determined by direct measurement, a check on the head produced by the known tilt was obtained. It was arranged that the pointer at the end of the spring lever indicated the head directly on the scale over which it moved and the head indicated was found to agree very well with that calculated from the weight obtained by means of the chemical balance as described above. The sensitivity of the apparatus when balanced on its knife-edges was represented by about 0·2 grm. at the chemical balance when the apparatus was immersed in oil.

Position of Spring for Constant Head.—The position of the spring to give constant head having been calculated, it was checked in the following manner: The head was set to a definite amount by tilting the viscometer so that the pointer moved upwards. After a short period of rest in this position with the main valve and by-pass valve open, the main valve was shut and the viscometer levelled, the pointer being then at zero, and the mercury standing higher in the right-hand tube than in the left-hand one.

The spring was now placed in the position previously calculated and set by means of the scales provided on the lever and beam above, and its tension adjusted to support the viscometer (it being arranged that the *left*-hand side should be the heavier) with the pointer at zero, the viscometer being on its knife-edges. The apparatus was fixed in this position (level), and the main valve opened to allow the mercury to again level itself, after which the valve was closed. On releasing the arrester, the extra weight of mercury then on the left-hand side caused the viscometer to tilt against the action of the spring. If the latter was in its correct position, the pointer, on coming to rest, should be as far below zero as it was above it when the head was set, the head being now solely due to the tilt of the apparatus as indicated by the pointer on the scale.

In short, when the tension of the spring was adjusted and the apparatus level, the head was produced by virtue of the position of the levels of the mercury in the tubes, and at the end of the check the mercury was in its "level" position with regard to the apparatus, but the tilt of the apparatus produced the same head as before.

Calculation of the Position of Spring from the Axis of the Apparatus.

Let Δ represent the density of the mercury, and
ρ the density of the liquid under test.
A the area of cross-section of the side tubes.
a the force in grammes necessary to tilt the apparatus for 1 cm. head (no flow taking place).
L the distance from the axis of the vertical side tubes to the axis of the apparatus.
l the distance of the spring from the axis of the apparatus.
S the stiffness of the spring in grammes per cm.

Then the increase in weight at the distance L from the axis due to 1 cm. head

$$= [(\Delta - \rho)\mathrm{A} - a] = \mathrm{K}.$$

If the spring were placed at a distance L from the axis, its stiffness would need to be such that a force K would cause it to extend 0·5 cm., *i.e.*, its stiffness would need to be equal to 2K grm. per centimetre length.

The distance of the spring from the axis, in order that its effective stiffness at a distance L should be equal to 2K, is therefore given by

$$l = \mathrm{L}\sqrt{\frac{2\mathrm{K}}{\mathrm{S}}}.$$

The apparatus was not very sensitive to the position of the spring.

Method of Experiment.—In carrying out an experiment, the pressure in the viscometer was applied by means of a small hand pump and intensifier. The pressure was measured by a dead-weight pressure gauge. After closing the valve or stop-cock on the viscometer, the intensifier was disconnected and the viscometer tilted to obtain the desired head, after which the flow valve and by-pass were shut and the apparatus levelled. The spring being placed in position, its tension was adjusted to support the viscometer in the level position, the pointer being at zero. Before these operations, the temperature of the bath and viscometer had been adjusted to the required value.

The flow valve was next opened, and time readings of the passage of the pointer over the scale were taken.

The volume of oil passing through the capillary in a certain time is obtained, as previously described, by the product of the cross-sectional area of one side tube and half the fall of the pointer during that time.

Method of Application and Measurement of Pressure.—The liquid for experiment was contained in a reservoir, from which it was led to a small hand pump, and thence to a pressure intensifier. The intensifier was connected to the viscometer by an easily detachable pipe of fine bore. After the pressure had been applied to the viscometer and the stop-cock closed, the connecting pipe was detached, so that the viscometer should be free to swing on its knife-edges. The hand pump served both to fill the viscometer with the liquid to be tested and to prime the intensifier.

The latter consisted of a steel plunger 1 cm. diameter, working in a strong steel cylinder. The plunger was guided axially by rigid bars, and its motion in the cylinders was produced by means of a screw, nut, and hand-wheel. The stroke of the plunger was about 10 diameters.

The cylinder carried a Bourdon pressure gauge, and a column fitted at the top with a small vertical piston and cylinder for the measurement of the pressure. The pressure side of the small piston and the pressure gauge communicated with the back end of the intensifier cylinder.

The piston was one hundredth of a square inch in sectional area, and could support, by means of a frame, a maximum dead weight of 224 lbs., corresponding to a pressure of 10 tons per square inch, or 1575 kgrm. per square centimetre.

It was arranged that the piston could be rotated to minimise its friction in the cylinder. The readings of the pressure gauge served as a check on the pressure measurement.

RESULTS OF EXPERIMENTS.

The Determination of the Viscosity of Water as a Check on the Accuracy of the Instrument.

The viscosity of water was determined at temperatures of 20° C. and 40° C. for comparison with the results of previous experimenters, and the following results were obtained :—

Temperature, ° C.	Capillary.			Head of mercury (cm.).	Time for pointer to fall 2 cm. (secs.).	Density of water.	Value of absolute coefficient of viscosity.
	No.	d^4 (cm.^{4}).	Length (cm.)				
20 ·0	1	$2{\cdot}493 \times 10^{-6}$	46 ·7	4 ·60	236 ·0	0 ·998	0 ·0099
40 ·0	1	$2{\cdot}493 \times 10^{-6}$	46 ·7	4 ·67	161 ·5	0 ·992	0 ·0070

(Cross-sectional area of the vertical tubes taken as 1 ·767 sq. cm.)

Previous determinations have been :—

Thorpe and Rodgers	0·010015 at	20° C.
Poiseuille	0·01008	20° C.
Sprung	0·01003	20° C.
Slotte	0·01008	20° C.

The Tests on Lubricating Oils—The oils tested were good commercial samples of their kind, and included vegetable, animal, fish, and mineral oils. The vegetable oils were represented by castor and rape, the animal by "trotter" (a substitute for lard oil), the fish by sperm, and the mineral by F. F. F. Cylinder, Victory Red, Bayonne, Mobiloil "A" and Mobiloil "BB."

The values of the kinematical viscosity obtained for pressures up to 1250 kgrm. per square centimetre are given in Tables II to V inclusive.

Table II.—Viscosity of Victory Red Oil (Mineral). No. 5 Capillary Tube, Length 44·8 cm. Temperature 40·0° C. Head 4·88 cm.

$$\text{“K”} = \frac{\eta \text{ at high pressure}}{\eta \text{ at atmospheric pressure}}.$$

Pressure (kilogrammes per sq. cm.).	Time for pointer to fall 2 cm. (seconds).	Specific gravity, ρ.	Kinematical Viscosity, η/ρ.	Absolute Viscosity, η.	K.
0	318	0·9290	1·905	1·77	1·00
157·5	484	0·9360	2·895	2·71	1·535
315	836	0·9428	5·00	4·715	2·665
472·5	1440	0·9493	8·605	8·17	4·62
630	2460	0·9552	14·69	14·03	7·935
787·5	3776	0·9612	22·55	21·68	12·26
945	6000	0·9668	35·80	34·61	19·58

Table III. — Viscosity of Castor Oil. Temperature 40·0° C. (No. 5 Capillary Tube used.)

Pressure (kilogrammes per sq. cm.).	η.	K.
0	1·82	1·00
23·94	1·875	1·03
227·6	2·48	1·365
550·5	4·18	2·295
864·6	6·60	3·625
1164	9·565	5·255

(Using No. 4 Capillary Tube.)
Atmospheric pressure, η = 1·85.

Table IV.—Viscosity of Mobiloils "A" and "BB." Temperature 40·0° C.

Pressure (kilogrammes per sq. cm.).	Mobiloil "A." (mineral).		Mobiloil "B.B." (mineral).	
	η.	K.	η.	K.
0	0·495	1·00	1·415	1·00
74·25	0·578	1·17	1·495	1·055
227·6	0·755	1·525	2·175	1·54
550·5	1·519	3·07	5·01	3·545
710·2	—	—	8·30	5·875
864·6	3·355	6·78	15·89	11·245
1019	5·105	10·31	37·40	26·47
1134	7·630	14·8		
1164	10·950	22·1		

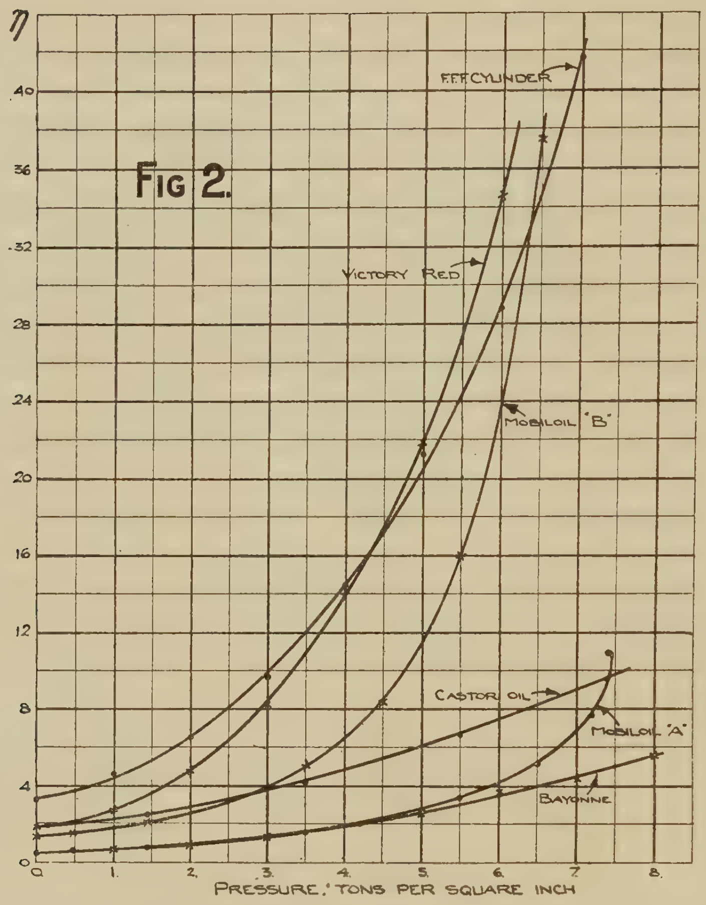


Fig 2.

Table V.—Viscosity of various Lubricating Oils. Temperature 40·0° C.

Pressure (kilogrammes per sq. cm.).	Bayonne oil (mineral).		FFF Cylinder oil (mineral).		Trotter oil (animal).		Rape oil (vegetable).		Sperm oil (fish).	
	η.	K.	η.	K.	η.	K.	η.	K.	η.	K.
0	0·47	1·00	3·24	1·00	0·344	1·00	0·375	1·00	0·154	1·00
157·5	0·62	1·315	4·53	1·40	0·413	1·20	0·422	1·125	0·190	1·23
315·0	0·92	1·96	6·48	2·00	0·550	1·60	0·539	1·44	0·236	1·535
472·5	1·32	2·81	9·71	3·00	0·686	1·995	0·703	1·875	0·229	1·94
630·0	1·86	3·96	14·45	4·46	0·824	2·395	0·880	2·345	0·368	2·39
787·5	2·51	5·34	21·33	6·59	—	—	1·089	2·905	—	—
866·2	—	—	—	—	—	—	—	—	0·483	3·135
945	3·65	7·77	28·80	8·895	1·217	3·535	1·310	3·495	—	—
1102·5	5·32	11·32	41·65	12·86	—	—	1·578	4·21	0·619	4·02
1260	7·55	16·07	—	—	1·731	5·03	—	—	—	—

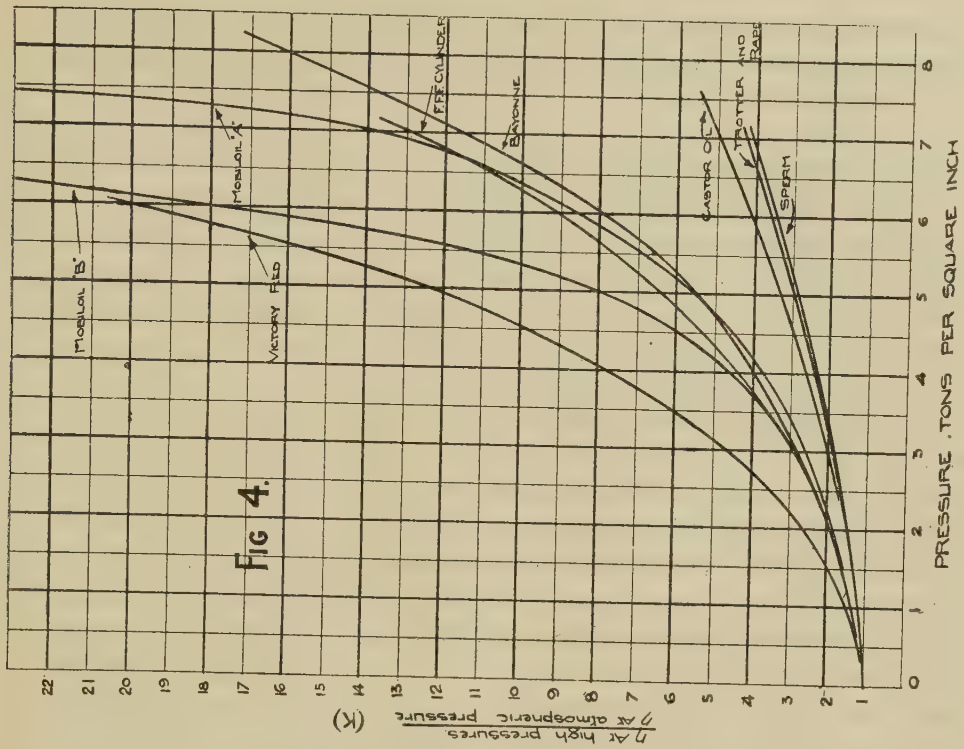

MOBILOIL 'B'
MOBILOIL 'A'
VICTORY RED
F.F.F. CYLINDER
BAYONNE
CASTOR OIL
TROTTER AND RAPE
SPERM
η At high pressures / η At atmospheric pressure (K)
22
21
20
19
18
17
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
1
2
3
4
5
6
7
8
PRESSURE . TONS PER SQUARE INCH

FIG 4.

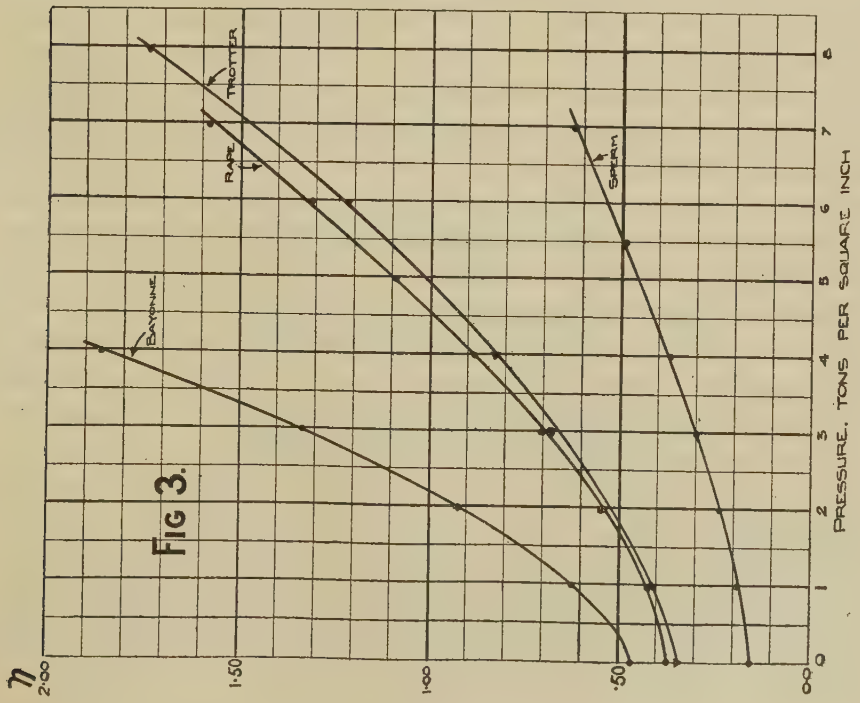

η
2·00
1·50
1·00
·50
0·0
BAYONNE
RAPE
TROTTER
SPERM
0
1
2
3
4
5
6
7
8
PRESSURE. TONS PER SQUARE INCH

FIG 3.

It will be observed that the experiments at atmospheric pressure were made on the castor oil with the capillary tubes of different sizes, viz., tubes Nos. 4 and 5.

PART II.—*Apparatus for the Determination of the Compressibility of Liquids, and the Values Obtained for Water and Certain Lubricating Oils.*

On the conclusions of the experiments described in Part I, for the measurement of the values of the kinematic viscosities of fluids, the work in connection with the estimation of the densities at high pressures was commenced, in order that the ratio of variation with pressure of the absolute viscosities of the oils might be obtained.

For this purpose a special apparatus was devised by the author, by means of which the compressibility of a liquid, under the pressures used in the viscosity tests, could be easily and rapidly measured.

The apparatus consists essentially of a small strong steel cylinder, about 50 diameters long, closed at one end, and fitted with a plunger, carrying a sleeve, at the other. The cylinder is filled with the liquid under experiment, and it is arranged that the plunger stands inside the cylinder for about 8 diameters, or half its length, at the commencement of the experiment. The whole is immersed in a strong tube of the liquid, and the pressure in this tube is raised to the desired value. The motion of the plunger necessary to equalise the pressure inside and outside of the small cylinder causes a movement of the sleeve relative to the plunger. The sleeve is provided with springs, which cause it to remain in its new position on the plunger, when the pressure is released and the latter moves to its original position relative to the cylinder.

Measurements are made of the position of the sleeve on the plunger before and after the application of the pressure, and the decrease in volume of the liquid in the small cylinder thus determined.

The steel cylinder was approximately 8 mm. bore, 16 mm. outside diameter, and 350 mm. long, closed at one end by a plug fitted with a small valve. The bore of the cylinder was very accurately cylindrical and straight. Its mean diameter was measured to within 0·0005 cm., and the depth of the bore to the face of the plug to within 0·002 cm. The capacity was checked by weighing the mercury content and by calculation from the dimensions.

The plunger consisted of a plain steel rod without packing of any kind, and was ground and lapped to a very good fit in the cylinder. The length of the plunger was about 12 cm. and it was always arranged that at least 5 cm. of its length was inside the cylinder during an experiment.

The sleeve was approximately 7 cm. in length and made a good sliding fit in the plunger, the tightness depending on the adjustment of the springs which pressed on the plunger, when in position, through slotted holes in the side of the sleeve.

The top of the small cylinder, the ends of the plunger and the ends of the sleeve, were all ground and lapped square with the axis of the cylinder.

The pressure vessel consisted of a strong steel tube 5 cm. outside diameter and 2 cm. bore, closed permanently at one end and provided at the other with a screwed plug for the admission of the apparatus and for connection to the pressure intensifier. This vessel was supported in an oil bath, the temperature of which could be maintained to within 0·1° C. The bath was fitted with a thermosyphon and a mechanical stirrer and the heat supply was regulated by a thermostat.

Measurements of the position of the plunger relative to the cylinder and sleeve were made by means of a depth micrometer. It was usually arranged that the top of the plunger was either flush or just below the top of the sleeve when the zero position was measured. After the application of the pressure, the sleeve was locked on the plunger before the new measurement was taken.

A perforated brass cup fitted over and protected the sleeve and plunger during the operations of immersion in and removal from the pressure vessel The accuracy of the determination of the volume of the cylinder with the plunger entered by a known distance is within 0·01 cm. The readings of the micrometer are probably accurate to about 0·002 cm.

The diagrams on fig. 5 illustrate the method of experiment.

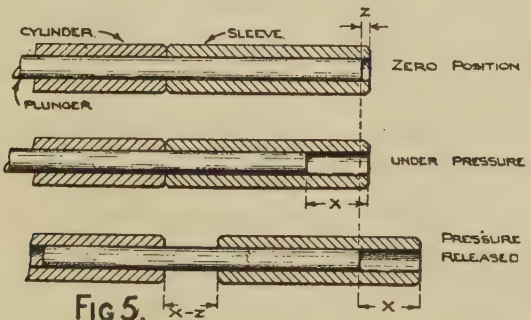


FIG 5.

Results of Preliminary Experiments with Water.—Distilled water, boiled to get rid of the dissolved air, was used. The plunger of the apparatus was smeared with castor oil to ensure that there should be no leak of air into the cylinder, past the plunger, if the latter was slightly pulled out accidentally.

The first experiments were made without the use of the bath at a temperature of 18° C. The room temperature had been constant at 18° C. for about one hour previous to the experiments being made.

The volume of the cylinder, with plunger and sleeve in position and with the top of the plunger flush with the top of the sleeve, was determined by calculation from the weight of the mercury content and found to be 15·56 c.c. This volume was checked by calculation from the dimensions of the several parts. The equivalent length of the cylinder, of uniform diameter, 0·768 cm., with plunger and sleeve in position at 18° C., was 33·75 cm. or 13·290 inches. The dimension is converted to inches because readings of the micrometer were in inches.

Tables VI and VII give the results obtained, which are compared with the results of Parsons and Cook for water under the same conditions, and it will be seen that very fair agreement exists between the results of the two investigations.

Table VI.—Compressibility of Water. Room Temperature 18·0° C.

$\rho = 0·9986$ at 18·0° C.

Pressure (kilogrammes per sq. cm.).	Micrometer measurement (inches).		Length of column of liquid (inches).		Ratio A/B.	Value of ρ.
	Initial "Z."	Final "X."	Initial "A."	Final "B."		
138·6	0·0590	0·1270	13·2310	13·163	1·0052	1·0040
299·2	0·0160	0·1715	13·2740	13·1185	1·0120	1·0160
338·6	0·0190	0·1900	13·2710	13·1000	1·0131	1·0118
456·7	0·0110	0·2525	13·2790	13·0375	1·0186	1·0172
611·1	0·0120	0·3330	13·2780	12·8570	1·0250	1·0236
771·7	0·0175	0·4040	13·2725	12·8860	1·0300	1·0285
926	0·2170	0·6880	13·0730	12·6020	1·0375	1·0361
1080	0·1530	0·6820	13·1370	12·6080	1·0421	1·0407
1235	0·0095	0·6161	13·2805	12·4740	0·0481	1·0468
1361	0·0275	0·6720	13·2625	12·4180	1·0513	1·0500
1543	0·0065	0·7290	13·2835	12·5610	1·0580	1·0565
1707	0·0075	0·7915	13·2825	12·4985	1·0630	1·0615

These results have been plotted and the following values of the compressibilities obtained:—

Table VII.—Temperature 18·0° C.

Pressure (kilogrammes per sq. cm.).	100	300	500	700	900	1100	1300	1500	1700
Compressibility $C \times 10^6$ per megabar	40·8	40·5	40·2	39·35	39·1	38·0	37·3	36·3	35·2
Compressibility $C \times 10^6$ (values obtained from Parsons' and Cook's results)	41·8	40·8	40·75	40·2	39·65	38·5	38·4	37·8	35·85

After the preliminary tests were made, the apparatus was slightly modified chiefly in the length of the cylinder and the arrangements for handling it, and the experiments were continued with the use of the constant temperature bath

The equivalent length of the modified cylinder of uniform diameter, 0·7685 cm., was 11·825 inches at 20° C. temperature.

As a check on the accuracy of the determinations of the compressibilities, a rod of steel of known volume could be introduced into the cylinder, reducing the internal volume by about 50 per cent., and the experiments were made both with and without the steel rod in place.

In order to compare the two results obtained a small correction was made for the reduction in volume of the steel rod due to the pressure and for this correction the value of the compressibility of steel was taken as $6·2 \times 10^{-6}$ cub. cm. per cubic centimetre per megabar.

The measurements of the steel rod were obtained in a measuring machine.

The results obtained with and without the introduction of the steel rod are given in Table VIII.

Table VIII.—Compressibility of Water at 20·0° C. Comparison of Results obtained with and without the volume of the cylinder reduced by approximately 50 per cent. by the introduction into the cylinder of a steel rod of known dimensions. Specific gravity of water at atmospheric pressure and 20·0° C. taken as 0·9983.

Pressure (kilogrammes per sq. cm.).	Whole volume of cylinder.		Half volume of cylinder.	
	Value of ρ.	Value of "C" per megabar.	Value of ρ.	Value of "C" per megabar.
157·5	1·0048	42·25	1·0048	42·1
315·0	1·0120	43·6	1·0118	43·75
472·5	1·0183	42·45	1·0180	42·1
630·0	1·0245	41·45	1·0247	41·8
787·5	1·0305	40·5	1·0305	40·7
945	1·0364	39·7	1·0363	39·65
1102·5	1·0421	38·9	1·0422	39·05
1260	1·0476	38·1	1·0476	38·15
1417·5	1·0526	37·15	1·0533	37·65

It will be seen on comparing the values of C in the two series of experiments that there is very good agreement between them. This indicates that errors due to the alteration in internal volume of the cylinder owing to the pressure are very small, as was expected from the method of experiment.

The accuracy of the determinations appear, therefore, to depend chiefly on the accuracy with which the micrometer measurements can be made, and especially the initial measurement. The latter depends in a great measure on the freedom of the liquid from air, and, in a lesser degree, on the fit of the plunger in the cylinder. The initial micrometer readings were always taken with the cylinder, plunger and sleeve suspended vertically in the bath, the tops of the latter just projecting above the bath liquid, in order that the micrometer could be used. The valve at the lower end of the cylinder was used in running out the excess of liquid when the plunger had been entered, in order that the initial position of the latter could be adjusted. By inverting the cylinder, the valve also served as a means of helping to get rid of any air which might have been trapped by the plunger, the air thus confined rising through the liquid in the cylinder and passing out through the valve with the excess liquid.

Experiments on the Lubricating Oils.—The results obtained are given in Tables IX to XII, the values of both the density and the compressibility being given for various pressures. Curves of variation in density are given in fig. 6, on which figure is also plotted for comparison the corresponding curve for water. It will be seen that the rate of change of density with pressure is practically the same for all the liquids tested.

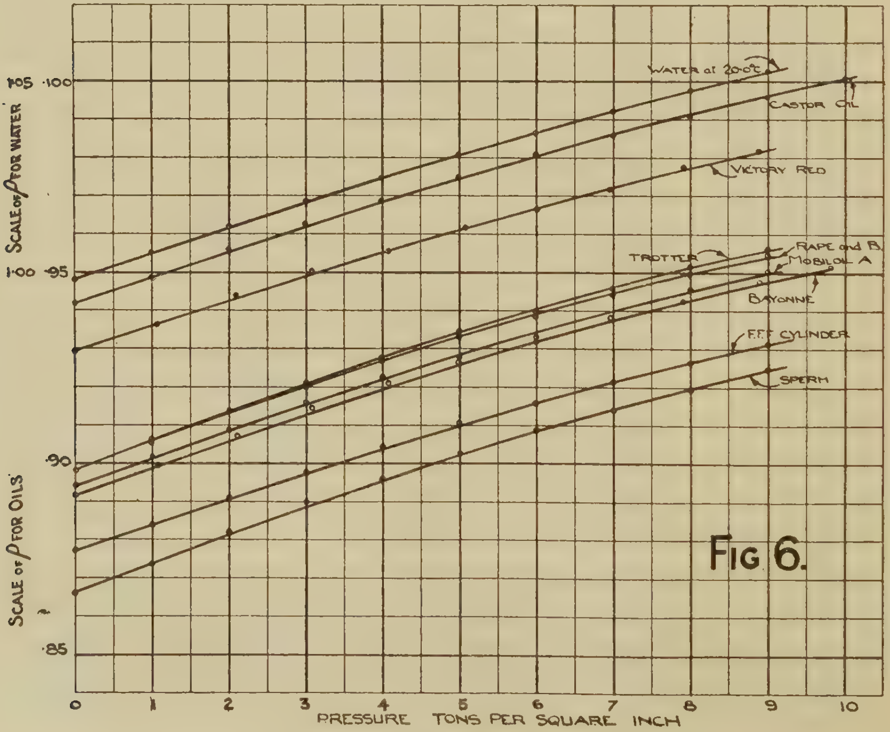


FIG 6.

Table IX.—Compressibility of various Lubricating Oils at 40·0° C. Temp. Compressibility "C" per megabar.

Pressure (kilogrammes per sq. cm.).	Castor oil.		Trotter oil.		Rape oil.		Sperm oil.	
	Value of ρ.	Value of C.	Value of ρ.	Value of C.	Value of ρ.	Value of C.	Value of ρ.	Value of C.
0	0·9414	—	0·8980	—	0·8980	—	0·8660	—
157·5	0·9488	50·5	0·9052	56·3	0·9058	55·7	0·8746	60·8
315	0·9558	48·6	0·9137	55·3	0·9129	52·1	0·8820	58·2
472·5	0·9625	47·0	0·9209	53·5	0·9199	51·1	0·8898	56·3
630	0·9686	45·3	0·9276	51·3	0·9270	50·5	0·8958	53·4
787·5	0·9748	44·5	0·9343	50·4	0·9330	48·2	0·9024	51·5
945	0·9808	43·2	0·9398	47·7	0·9381	46·0	0·9088	50·5
1102·5	0·9858	41·5	0·9456	46·3	0·9440	44·8	0·9136	48·1
1260	0·9906	40·1	0·9512	45·0	0·9496	43·6	0·9196	46·9
1417·5	0·9958	39·4	0·9560	43·4	0·9547	42·7	0·9249	45·7
1575	1·0010	38·3	—	—	—	—	—	—

Table X.—Compressibility of various Lubricating Oils at 40·0° C. Temp.—*contd.*

Pressure (kilogrammes per sq. cm.).	F.F.F. Cylinder oil.		Mobiloil "A."		Mobiloil "BB."	
	Value of ρ.	Value of C.	Value of ρ.	Value of C.	Value of ρ.	Value of C.
0	0·8770	—	0·8940	—	0·8990	—
157·5	0·8838	49·8	0·9011	51·1	0·9062	51·8
315·0	0·8908	50·8	0·9082	50·5	0·9136	50·8
472·5	0·8974	49·6	0·9159	50·9	0·9200	49·2
630	0·9042	48·2	0·9226	50·7	0·9264	47·7
787·5	0·9102	44·1	0·9275	46·6	0·9326	46·6
945	0·9158	45·5	0·9328	44·8	0·9380	45·0
1102·5	0·9212	44·4	0·9399	45·0	0·9434	43·6
1260	0·9262	42·9	0·9451	43·4	0·9490	42·6
1417·5	0·9310	41·6	0·9501	42·6	0·9540	41·4

Table XI.—Compressibility of Victory Red Oil. Temperature 40·0° C.

Pressure (kilogrammes per sq. cm.).	Value of ρ.	Value of C.
0	0·9290	—
158·5	0·9363	47·6
330·7	0·9439	48·4
485	0·9500	46·7
644	0·9555	43·8
798·5	0·9618	43·8
948	0·9667	41·9
1098	0·9716	40·3
1249	0·9772	40·0
1402	0·9817	38·8

Table XII.—Compressibility of Bayonne Oil. Temperature 40·0° C.

Pressure (kilogrammes per sq. cm.).	Value of ρ.	Value of C.
0	0·8914	—
166·9	0·8986	51·3
330·7	0·9070	52·1
485	0·9145	51·3
644	0·9204	48·9
787·5	0·9262	48·6
948	0·9320	46·3
1098	0·9379	46·2
1249	0·9424	44·2
1402	0·9474	43·1
1548	0·9515	41·8

General Remarks on the Results of the Tests on Lubricating Oils.

The calculated values of the coefficient of absolute viscosity (η), obtained from the values of the kinematic viscosity (η/ρ) and of the density (ρ), determined by experiment, are given in Tables I to IX. The values of η are shown plotted against the pressure in figs. 2 and 3. It will be noted that the scale of ordinates of fig. 2 is twenty times that of fig. 3.

The curves show that the viscosity increases with pressure, and at an increasing rate as the pressure rises.

Extreme care in the measurement of the pressure had to be taken, especially in the cases of the mineral oils, in which, at pressures above 800 kgrm. per square centimetre, the rate of change of viscosity with pressure is very great.

A better comparison between the results obtained is made by plotting the values of K against the pressure, where K is the ratio of the absolute viscosity under high pressure to the absolute value at atmospheric pressure. The values of K are given in the final columns of Tables I to IX, and are plotted in fig. 4.

The curves of the latter figure show a difference between the fixed and the mineral oils. The mineral oils vary considerably among themselves and generally have a high rate of increase in viscosity with pressure. The fixed oils, however, do not greatly differ from each other and show an increase in viscosity at 1000 kgrm. per square centimetre to approximately four times their values at atmospheric pressure, compared with anything between ten and twenty-five times the corresponding values for the mineral oils.

The experiments were carried out in the Engineering Department of the

National Physical Laboratory, and the whole of the apparatus was constructed in the workshops of the department.

In conclusion, the author desires to express his thanks to the Committee on Lubrication and Lubricants of the Department of Scientific and Industrial Research, and to Sir Richard Glazebrook and Dr. T. E. Stanton, for the interest taken in the progress of the work.

A Study of Catalytic Actions at Solid Surfaces.—III. *The Hydrogenation of Acetaldehyde and the Dehydrogenation of Ethyl Alcohol in Presence of Finely-divided Metals.*

By E. F. Armstrong, D.Sc., F.I.C., and T. P. Hilditch, D.Sc., F.I.C.

(Communicated by Prof. H. E. Armstrong, F.R.S.—Received March 2, 1920.)

Until recently, alcohol was always produced by fermenting saccharine materials; acetic acid was obtained as a by-product in making charcoal; acetone was prepared by heating calcium acetate. During the war, both acetic acid and acetone were called for in quantities far larger than would be supplied by such methods; alcohol was also in special demand in connection with the manufacture of cordite; now it is coming into prominence as a possible motor fuel. The effect has been to bring synthetic processes of preparing such compounds to the fore; it is interesting that the methods introduced have nearly all been devised by French chemists.

As far back as 1863, Berthelot was able to show that ethylene obtained from alchohol could be reconverted into alcohol by absorbing the gas in sulphuric acid. The direct synthesis of alcohol from inorganic materials was accomplished when he obtained acetylene by combining carbon with hydrogen at the temperature of the electric arc, as it was possible to hydrogenate acetylene to ethylene.

Berthelot was also the first to attempt the hydration of acetylene, effecting this by the action of sulphuric acid, followed by that of water. Acetaldehyde and crotonic aldehyde were thus produced with other products.

Subsequently it was found that mercuric salts cause a rapid hydration of acetylene to aldehyde in presence of warm dilute sulphuric acid; this discovery has rendered possible the more recent technical processes for manufacturing aldehyde from acetylene.

A simple method of producing acetylene having been provided by the discovery of calcium carbide, the synthetic manufacture of alcohol is now within the range of economic practice, at all events in regions where cheap water power is available.

Alcohol is already being made in Switzerland by the reduction of acetaldehyde by hydrogen in presence of nickel, according to Sabatier's process. The aldehyde is obtained from acetylene by a continuous process of hydration.

Early in the war, a process of manufacturing aldehyde was developed at Messrs. Joseph Crossfield and Sons, Warrington, involving the application of Sabatier's discovery that alcohol is resolved into this compound and hydrogen when passed over heated copper, preferably at about 300 °C.* Many hundreds of tons were produced and converted into acetic acid and acetone, the yield under favourable conditions amounting to 90 to 93 per cent. calculated on the alcohol used. From 20 to 25 per cent. of the alcohol is converted at each passage over the metal into an equimolecular mixture of aldehyde and hydrogen. To obtain the former, the vapours are cooled and then passed into an elaborate fractionating column, in which the aldehyde is separated from hydrogen and the excess of alcohol The technical product contained at least 97 per cent. of aldehyde.

In continuation of our studies of catalytic action at solid surfaces, the dehydrogenation of alcohol and the hydrogenation of aldehyde have both been submitted to careful examination; in the present communication, we desire to draw attention to certain peculiarities in the interactions.

Hydrogenation of Aldehyde.—Aldehyde may be converted into alcohol by passing the vapour, together with hydrogen, over either copper or nickel (Sabatier); but in presence of the latter metal, probably owing to the special affinity of nickel for the carbonyl group, the aldehyde is prone to undergo decomposition into carbon monoxide and methane.

The following are the results of experiments in which the ratio of hydrogen to aldehyde was varied from 1·5 to 2·5 molecular proportions of the former to one of the latter.

Table I.

Catalyst.	Temperature.	Vapour hydrogenated.		Time.	Gas-volume change.	Aldehyde recovered.	Alcohol.	
		Aldehyde.	Hydrogen.				Weight.	Yield.
	°C.	grm.	litres.	hours.	litres.	grm.	grm.	per cent.
Nickel...	120–150	135	120	5	—	49	47	53·6
Copper...	200–210	127	155	3½	34 diminution	40	76	87·6
Copper...	300	114	100	2	5 expansion	34	27	33·7

It is to be noted that aldehydes are more slowly reduced than are the corresponding simple ethylenic compounds. Apart from this, the hydrogenation is comparable with that of an olefinic derivative in presence of nickel or copper and the mechanism of the change is to be considered as identical with that of the latter process.*

In the experiment with copper at 300°, the amount of alcohol obtained should have involved the withdrawal of about 14 litres of hydrogen; actually, an expansion amounting to about 5 litres was observed, so that about 19 litres of gaseous products of decomposition was obtained. A snap-sample of the gas contained 2 per cent. CO_2, 2·6 per cent. olefines, 3·7 per cent. CO and 3·7 per cent. calculated to be methane. If the point of equilibrium reached had been the same as in proceeding from the dehydrogenation side, about 85 grm. of alcohol should have been produced; at least, it might have been expected that the amount of aldehyde recovered would have been less than that of the alcohol formed.

Dehydrogenation of Alcohol.—The results of typical experiments, using 92 per cent. alcohol, are given in Table II.

The yield of aldehyde isolated compared with that corresponding to the volume of hydrogen measured is given as a percentage in the final column "Ratio $CH_3.CHO : H_2$."

Table II.

Catalyst.	Temperature.	Alcohol passed.		Time.	Gas evolved.		Aldehyde obtained.	Ratio $CH_3.CHO : H_2$.
		Grm.	per cent. EtOH.		Litres.	per cent. H_2.		
	°C.			hours.				per cent.
Nickel ...	240–260	945	92	2	121	60	50	35·7
Copper...	300	289	92	1	41	96	72	96
Copper...	295–300	595	92	2	82	98·3	156	97

In the experiment with nickel, the gas evolved contained 60 per cent. H_2, 20 per cent. CO, 15–17 per cent. methane.

In the case of copper, not only is the ratio of aldehyde to hydrogen close to that calculated but the unchanged alcohol may be recovered almost quantitatively, the yield of aldehyde being about 90–95 per cent. of that to be expected from the amount of alcohol used. There is a striking absence of the secondary products observed when aldehyde together with an excess of hydrogen is passed over the metal at the same temperature.

Nor is the difference to be accounted for by the presence of water in the former case. The alcohol in the experiments recorded in the following Table III had been as fully deprived of water as possible by repeated distillation over fresh lime and finally over sodium; the copper had been heated in a current of dry hydrogen at 300° during several hours. The difference in the gaseous products in presence and absence of water should be specially noted.

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* *Cf.* 'Roy. Soc. Proc.,' A, vol. 96, pp. 137, 322 (1919).

Table III.

Alcohol passed.		Temperature.	Time.	Gas evolved.						Aldehyde obtained.	Ratio $CH_3CHO:H_2$.
				Litres.	Per cent. analysis.						
Per cent. EtOH.	Grm.				H_2.	CO_2.	C_2H_4.	CO.	"CH_4."		
		°C.	hours.								per cent.
Anhydrous	150	300	1	30	76·6	2·4	0·7	3·5	8·7	28	67
92	130	300	1	24	91·0	1·5	0·3	Nil	4·0	38	95
92	2080	330–335	7	582	97·1	—	—	—	—	610	55
92	315	325–330	2	73	98·9	—	—	—	—	95	67
75	855	325–330	3	58	98·0	—	—	—	—	93	83
50	2195	325–330	6	117	91·7	—	—	—	—	176	83

It is evident, (*a*) that the presence of water improves the yield of acetaldehyde relatively to that of hydrogen. (*b*) Using alcohol of a given concentration (*e.g.*, 92 per cent.), as the temperature is raised the yield of aldehyde is considerably lessened, although the amount of alcohol decomposed and the volume of hydrogen produced are much increased (at 300° the proportion of alcohol attacked is about 50 per cent. of the total quantity passed as against 20–25 per cent. at 300°). (*c*) At the higher temperature, the yield may be partially restored by using alcohol containing a larger proportion of water. (*d*) Even at 300°, if alcohol rendered as anhydrous as possible be used, the yield falls very seriously.

Whatever the conditions, small quantities of by-products are always produced, notably *n*-butyric aldehyde, crotonic aldehyde and ethyl acetate, the total amount being normally of the order of 1 or 2 per cent. of the aldehyde formed.

The results obtained on merely passing aldehyde together with water vapour over heated copper at 300° are recorded in the following Table:—

Table VI.

Vapour passed.		Products obtained after passing over Cu catalyst at 300°.					Total percentage.	
Water.	Aldehyde.	Aldehyde.	Ethyl acetate.	$C_3H_7.CHO$.	Alcohol.	$CH_3.COOH$.	Accounted for as aldehyde.	Loss of aldehyde.
125	95	77	0·65	0·7	2·2	1·8	80·6	15·1
120	138	102				1·3	105	24·0
10	91	46	0·5	1·8	1·2	0·8	50	45·0

The proportion of by-products in these experiments is of the order obtained in the actual dehydrogenation of alcohol on the large scale and is not materially affected by the amount of water present. It is clear that water has a considerable protective influence on the aldehyde. To determine whether this protective action extended so far that the reverse action involved in hydrogenation were equally favoured by water, the following experiments were instituted :—

Table V.

Vapour passed.			Gas products obtained after passing over Cu catalyst at 300°.						Loss of aldehyde.
H_2.	H_2O.	Aldehyde.	Expn.	Aldehyde.	Ethyl acetate.	$C_3H_7.CHO$.	Alcohol.	$CH_3.COOH$.	
lit.	grm.	grm.	lit.						per cent.
40	100	86	0·45	66	0·4	1·5	3·6	1·9	15·1
40	20	79	0·10	31	0·5	2·2	3·3	1·0	51·9

The results show that whilst the aldehyde is protected from decomposition, the effect of even a small proportion of water is to retard hydrogenation considerably—in fact, to render it almost negligible.

Sabatier has attributed the dehydrogenation of alcohol as well as of hydrocarbons by finely divided metals to the supposed aptitude of such metals to form hydrides, the attraction of the metal for hydrogen being regarded as the impelling force.

But it is obvious that the relative affinities of all the agents concerned in such interactions must come into play. In the case of aldehyde, we are inclined to regard the affinity of the carbon compound rather than that of the hydrogen to the metal as of prime importance, indeed, as the determining factor; the marked influence of the metal in causing secondary decomposition is in itself a clear indication that the attraction exercised upon the aldehyde at the metallic surface is considerable.

The protection afforded by water in the dehydrogenating process may be ascribed, from this point of view, to the influence it exercises on the removal of the molecules of aldehyde from the sphere of action. That it has not been found to exercise a corresponding influence on the reverse process is perhaps due to the fact that the conditions cannot well be made the same in the two cases; in other words, the behaviour of a surface at which the aldehyde is being produced towards hydrogen and water may well be different from that of a surface saturated with water towards a mixture of aldehyde and hydrogen.

The general explanation of the changes studied appears to us to be the same as that suggested in our previous communications with reference to simple ethylenic compounds.

The same considerations apply equally to those metallic oxides which have been shown by Sabatier to act similarly to (though less vigorously than) copper on alcohols; the views of earlier workers have involved a mechanism of interaction different in the case of metals from that of metallic oxides; such difference is most unlikely to occur.

Our present hypothesis correlates the action of dehydrogenating metals and metallic oxides with those which are either both dehydrogenators and dehydrators or are exclusively dehydrating in their action; the primary action of the catalyst in all these cases is to effect an association with the carbon compound, the resulting unstable complex then being resolved into other compounds.

A Study of Catalytic Actions at Solid Surfaces.—IV. *The Interaction of Carbon Monoxide and Steam as Conditioned by Iron Oxide and by Copper.*

By E. F. ARMSTRONG, D.Sc., F.I.C., and T. P. HILDITCH, D.Sc., F.I.C.

(Communicated by Prof. H. E. Armstrong, F.R.S. Received March 18, 1920.)

The process summed up in the equation

$$CO + H_2O \rightleftarrows CO_2 + H_2 + 10{,}200 \text{ cal.}$$

is limited by the conditions which govern any homogeneous system in equilibrium: if the concentration of carbon monoxide, water, carbon dioxide, and hydrogen be denoted by a, b, c, d respectively, by the usual application of the law of mass action

$$k_1 ab = k_2 cd,$$

or

$$K = k_2/k_1 = ab/cd.$$

The value of K, the "equilibrium constant," depends on the temperature at which interaction takes place.

Haber* gives the following experimental values of K between 200° C. and 600° C.:—

Temperature.	227°.	327°.	400°.	500°.	600°.
K	0·006	0·03	0·05	0·16	0·32

These values, of course, define merely the extreme limits of composition of the gas-mixture, by whatever intermediate steps the transformation be effected. As a matter of fact, a mixture of carbon monoxide and steam at any of the temperatures mentioned, in the absence of a third agent, would attain equilibrium only after an exceedingly long time. It is well known, however, that many metallic oxides accelerate the attainment of equilibrium, specially prepared oxides of iron being very effective; the interaction has been utilised in the manufacture of hydrogen, the first attempt being that made by the Badische Anilin und Soda Fabrik in producing hydrogen for the Haber ammonia synthesis.

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* 'Zeitschr. Physik. Chem.,' vol. 68, p. 731 (1909).

The action of the iron oxide may be represented as follows:—

$$(a)\begin{cases} CO + Fe_3O_4 \rightleftarrows CO_2 + 3FeO, \\ CO + FeO \rightleftarrows CO_2 + Fe, \end{cases}$$

$$(b)\begin{cases} H_2O + 3FeO \rightleftarrows Fe_3O_4 + H_2, \\ H_2O + Fe \rightleftarrows FeO + H_2, \end{cases}$$

or together

$$CO + H_2O + (Fe_3O_4 - FeO - Fe) \rightleftarrows (Fe_3O_4 - FeO - Fe) + CO_2 + H_2.$$

The action belongs to the same class as several others we have described in these papers, and may be regarded as proceeding by a series of chemical unions between the four agents and the iron oxide catalyst.

Our present object is to describe experiments which show that copper, specially prepared for use as a catalyst [the same material which served for our experiments (Part III of this series) upon the dehydrogenation of ethyl alcohol)], can also condition the transformation of carbon monoxide and steam into carbon dioxide and hydrogen. Whereas, however, iron oxide at a suitable temperature causes the action to proceed almost to the point of equilibrium, copper, even at its optimum temperature, does not effect more than 50–70 per cent. of the possible amount of chemical change; the exact proportion is to some extent a function of the composition of the mixture used.

These results are of considerable theoretical interest from the point of view of the general theory of catalysis which we have lately put forward, because they illustrate very beautifully the specific action of two different types of catalyst, effecting ultimately the same change ($CO + H_2O = CO_2 + H_2$), but, as we shall show, by an entirely different mechanism, involving the production of intermediate systems of quite distinct kinds.

At first sight, it might seem that the case was one in which no chemical change was involved, the process being in each instance merely due to physical adsorption or concentration of the acting gases at the active surface; but the evidence which we are about to quote on the relation of temperature to the amount of action produced is sufficient to negative this view.

It is obvious that copper cannot exercise the function we have elsewhere ascribed to iron oxide, as water has no detectable action on the copper catalyst, at all events up to 500° C.

Sabatier and Mailhe* have observed, on the other hand, that finely divided copper is capable of decomposing formic acid into carbon dioxide and hydrogen from 190° C. upwards, and our experiments go to show that it is this specific property of copper which accounts for the results we have obtained. Apparently, there is a tendency to the equilibrium

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* 'Compt. Rend.,' vol. 152, p. 1212 (1911).

$$CO + H_2O \rightleftarrows H.COOH,$$

the balance being overwhelmingly in favour of the uncombined components, as indicated; in presence of copper the formic acid is partially or wholly removed in the sense

$$H.COOH \longrightarrow CO_2 + H_2,$$

so that ultimately a large proportion of the carbon monoxide is transformed into dioxide.

It is well known, of course, that under quite different conditions carbon monoxide will yield formates; for example, under high pressure and at a moderate temperature, this gas may be readily absorbed by caustic alkalies.

Again, K. A. Hofmann* has explained the oxidation, at the ordinary temperature, of carbon monoxide to dioxide at a copper surface moistened with alkali by assuming the formation of a labile isoformate, HO.C.OK; the production of this substance is only minimal under ordinary conditions but is stimulated in presence of copper.

We have succeeded in proving that a mixture of carbon monoxide and steam, under the conditions of our experiments (at about 350° C.) but in the absence of any catalyst, may give rise to the momentary formation of small but quite detectable quantities of formic acid. Thus, when ammonia was added to the gases before passing through the heated tube, in the expectation that some ammonium formate might remain undecomposed at the exit of the apparatus, this hope was realised, the aqueous condensate from the apparatus being found to blacken silver nitrate and to reduce neutral mercuric chloride solution to mercurous chloride. The amount of formic acid preserved was, of course, quite minute. A similar result was obtained when the carbon monoxide and steam were passed over lime at 350° C.; details of these experiments are given after the main series of experiments with copper and iron oxide catalysts have been described.

We have been chiefly concerned to examine the amount of the change

$$CO + H_2O \rightleftarrows CO_2 + H_2$$

at temperatures from 200° C. to 500° C. with both copper and iron oxide catalysts. In order to standardise as far as possible the time-factor in the attainment of equilibrium, we have selected a rate of flow of gas such that the maximum change was effected over the most active range of temperature;

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* 'Ber.,' vol. 51, p. 1526 (1918).

we then arranged for the same rate of flow at the other temperatures and noted the amount of carbon monoxide converted to dioxide.

Two samples of gas were used in the course of the work:

(a) "95 *per cent. CO-gas*" obtained from sodium formate and sulphuric acid; this gas was operated at a rate of 12 litres per hour.

(b) "40 *per cent. CO-gas*" ordinary water-gas, used at the rate of 25 litres per hour.

In all cases a mixture of one volume of the gas with approximately 2·5 volumes of steam was passed over the catalyst, the water vapour being picked up by the gas during its passage through a vessel containing agitated water maintained at a temperature adjusted to give the desired saturation of the gas with steam.

The limiting value of the amount of carbon monoxide which can be transformed is derived as follows:—

Let a, b, c, d, as before, be the original concentration (volumes) of carbon monoxide, water, carbon dioxide, and hydrogen. Then, if a volume-concentration s of carbon monoxide interact with steam

$$K = \frac{(a-s)(b-s)}{(c+s)(d+s)}.$$

Hence the theoretical values of s can be determined at each temperature for which K is given and also the corresponding ratio

$$s/a = \textit{amount of CO changed/original amount of CO}.$$

In the actual experiments, the change was followed by analyses of the entering and issuing gases other than water.

Let the concentrations of CO_2, CO and H_2 per unit volume in the original gas be respectively X, Y, and Z, and let y of the original CO be changed. After re-condensation of the steam, the volume of the gas is now $1+y$, and we have

$$\text{New concentration CO} = \frac{Y-y}{1+y}.$$

$$\text{New concentration } CO_2 = \frac{X+y}{1+y}.$$

$$\text{New concentration } H_2 = \frac{Z+y}{1+y}.$$

Gas-analysis furnished experimental values for the old and new percentages of CO, CO_2 and H_2, the CO estimation being considered to be the most accurate of the three.

Thus, from the measured new per cent. CO

$$y = \frac{\text{Y} - \text{new per cent. CO}/100}{1 + \text{new per cent. CO}/100}$$

and experimental values were deduced for

$$y/Y = \textit{amount of CO changed/original amount of CO},$$

i.e., a figure comparable with the theoretical s/a above.

Further, an estimate of the accuracy of the analytical work was obtained by comparing the found and calculated new percentages of CO_2 and H_2 :—

$$\text{New per cent. } CO_2 \ (\textit{calculated}) = 100 \cdot \frac{X+y}{1+y}.$$

$$\text{New per cent. } H_2 \ (\textit{calculated}) = 100 \cdot \frac{Z+y}{1+y}.$$

I. 95 *per cent. CO—Gas.*

Composition of gas : 0·35 per cent. CO_2, 95·3 per cent. CO, 2·3 per cent. H_2.

The theoretical data for this gas are as follows :—

1 vol. gas + 2·5 vols. H_2O,

$$a = 0{\cdot}272, \quad b = 0{\cdot}714, \quad c = 0{\cdot}001, \quad d = 0{\cdot}007.$$

Temperature.	227°.	327°.	400°.	500°.	600°.
K	0·006	0·03	0·05	0·16	0·32
s	0·271	0·268	0·263	0·250	0·234
s/a	0·997	0·983	0·966	0·919	0·860

Experimental data :—

Temperature.	Composition of issuing gas.			y.	y/Y.	Per cent. CO_2.	Per cent. H_2.
	Per cent. CO_2.	Per cent. CO.	Per cent. H_2.			Calculated from y.	
	(*a*) Reduced copper catalyst.						
200°	3·1	87·0	5·3	0·044	0·046	4·6	6·4
250	23·9	48·3	23·5	0·317	0·333	24·3	25·8
300	41·4	14·0	41·5	0·713	0·748	41·8	42·9
350	43·4	14·0	39·5	0·713	0·748	41·8	42·9
400	40·5	15·5	41·2	0·691	0·725	41·0	42·2
500	35·2	24·2	37·0	0·572	0·600	36·6	37·9
	(*b*) Iron oxide catalyst.						
250	9·6	70·4	14·0	0·146	0·153	12·2	14·8
300	27·9	35·1	26·2	0·446	0·468	31·9	32·4
350	45·6	4·2	45·8	0·874	0·917	46·8	47·9
400	47·0	2·4	47·0	0·907	0·952	47·7	48·8

The relations of y/Y to temperature, together with the corresponding values for s/a, are shown graphically in fig. 1.

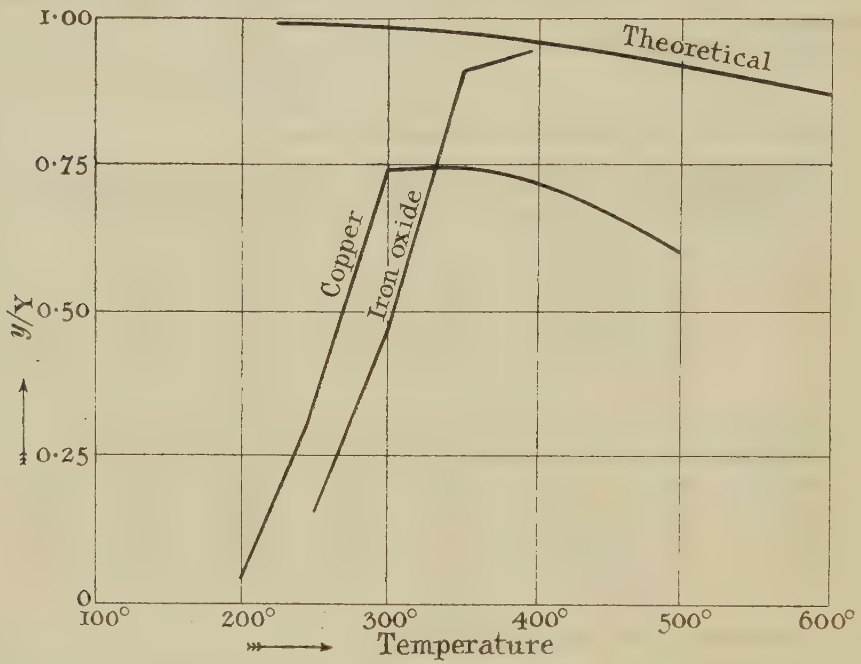

Fig. 1.

II. 40 *per cent. CO—Gas* (*Water-Gas*).

Average composition of gas: 5 per cent. CO_2, 40 per cent. CO, 47 per cent. H_2.

Theoretical data:—

1 vol. gas + 2·5 vols. H_2O.

$a = 0·114, \quad b = 0·714, \quad c = 0·014, \quad d = 0·134.$

Temperature.	227°.	327°.	400°.	500°.	600°.
K	0·006	0·03	0·05	0·16	0·32
s	0·1136	0·1129	0·1111	0·1065	0·0997
s/a	0·996	0·990	0·975	0·934	0·875

Experimental data :—

Temperature.	Composition of issuing gas.			y.	y/Y.	Per cent. CO_2.	Per cent. H_2.
	Per cent. CO_2.	Per cent. CO.	Per cent. H_2.			Calculated from y.	
(a) Reduced copper catalyst.							
Composition of gas used :— (i) 150–350° C....... 3·7 per cent. CO_2, 39·6 per cent. CO, 49·0 per cent. H_2. (ii) 400–500° C....... 5·3 per cent. CO_2, 39·0 per cent. CO, 46·7 per cent. H_2.							
150	3·8	39·2	47·6	0·002	0·005	3·9	49·1
200	4·0	39·4	49·8	0·001	0·002	3·8	49·0
250	9·9	31·2	52·8	0·064	0·162	9·5	52·1
300	14·0	23·7	57·0	0·129	0·326	14·7	54·8
350	17·1	19·9	56·4	0·165	0·416	17·3	56·2
400	15·8	20·3	53·9	0·155	0·398	18·0	54·2
500	18·6	20·3	52·8	0·155	0·398	18·0	54·2
(b) Iron oxide catalyst.							
Composition of gas used :—5·1 per cent. CO_2, 39·9 per cent. CO, 47·3 per cent. H_2.							
200	4·7	39·3	45·0	0·004	0·010	5·5	47·5
250	5·6	36·4	46·7	0·026	0·065	7·5	48·4
300	15·4	23·0	48·3	0·137	0·343	16·0	53·9
350	27·0	7·7	55·4	0·299	0·748	26·9	59·2
400	30·7	5·7	53·1	0·324	0·821	28·3	60·2

The results are given graphically in fig. 2.

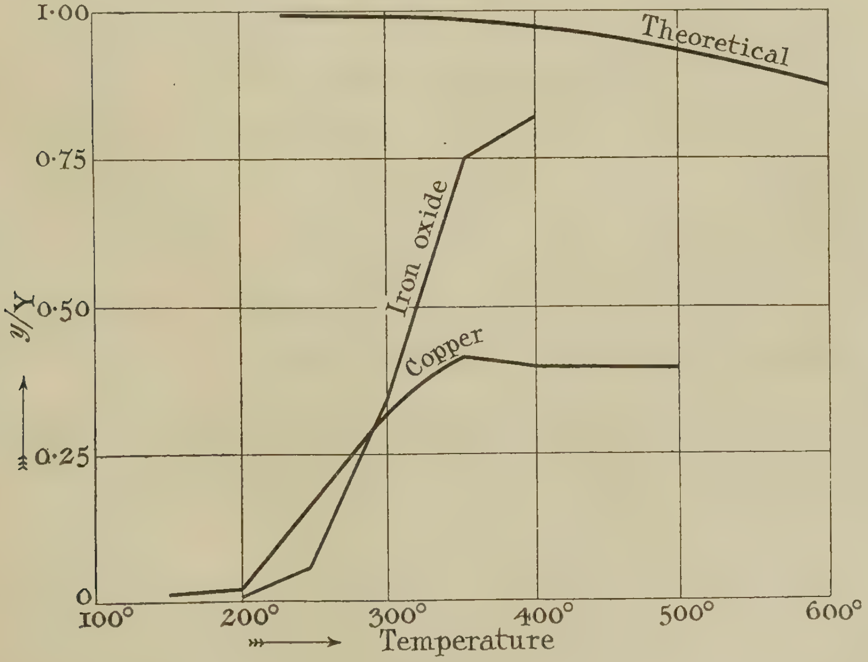

Fig. 2.

Copper is thus much less complete in its action than iron oxide at the higher temperatures; but over the range 200°–300° C. it is definitely more active than iron oxide; copper commences to act at a reasonable rate at about 220° C., whereas iron oxide is barely active at 250° C., is still slow at 300° C. and does not reach full activity until about 400° C.

We have seen that copper decomposes formic acid from 190° C.; on the other hand, the iron oxide process is dependent on the temperature ranges at which oxidation of carbon monoxide by iron oxide and decomposition of steam by iron or ferrous oxide occur at sufficiently rapid rates.

The oxidation of the monoxide by iron oxide proceeds at as low a temperature as 200° C.; but the decomposition of iron by steam is not a rapid action below about 400° C., although this figure refers to massive iron and would no doubt be somewhat lower for the more active iron or ferrous oxide produced by the oxidation of carbon monoxide in presence of steam.

It is evident that the relative activities of (*a*) copper and (*b*) iron oxide to carbon monoxide and steam at the lower ranges of temperature are closely parallel to their respective powers of decomposing (*a*) formic acid and (*b*) steam.

The amount of action effected by the copper catalyst declines somewhat after 350° C., and the maximum change effected appears to be greater the higher the proportion of carbon monoxide in the original gas.

It is not without interest that, although water is not decomposed *per se* by copper, we have observed signs on two occasions that water enters into an active association with this metal, thus:—

(i) The "protective" action of water on aldehyde and the suppression of hydrogenation of aldehyde in presence of water when copper is used as catalyst was explained (this series, Part III) on the hypothesis that water entered into association or was adsorbed preferentially to aldehyde at the copper surface.

(ii) In the present instance, we have a case in which water in association with copper actually takes part in a chemical action.

The following is a summary of the data obtained on passing water-gas (5·1 per cent. CO_2, 39·9 per cent. CO, and 47·3 per cent. H_2) with steam through a tube maintained at 350° C. in presence of ammonia or of lime:—

Experiment.	Alkali present.	Litres of water-gas.		Composition of issuing gas.		
		Passed.	Contraction.	Per cent. CO_2.	Per cent. CO.	Per cent. H_2.
1	Ammonia	50·0	2·15	2·0	37·4	48·5
2	„	50·0	2·85	2·5	37·5	47·3
3	Lime	40·0	2·40	3·1	36·1	50·8

The aqueous condensates from Experiment 2 were made slightly acid with hydrochloric acid and boiled with a solution of mercuric chloride, when 0·0369 gram of mercurous chloride was formed, corresponding to 0·0036 gram of formic acid.

The Theory of the Katharometer.

By H. A. Daynes, M.Sc., University of Birmingham.
(With an Introductory note by G. A. Shakespear.)

(Communicated by Prof. S. W J. Smith, F.R.S. Received January 5, 1920.)

[*Historical Note by G. A. Shakespear, M.A., D.Sc.*—In September, 1915, at the request of a member of the Board of Invention and Research of the Admiralty, I undertook to devise an instrument capable of giving automatic indication of the presence of hydrogen in small quantities (*e.g.*, 1 or 2 per cent.) in air. The well-known surface-action of palladium and platinum wires suggested itself as a phenomenon obviously adapted to the purpose. The wire was used as two arms of a Wheatstone bridge, one of these arms being protected from the gas by a thin glass tube, the other being exposed. When a sufficiently great current of electricity was passed through the bridge, the exposed arm rapidly increased in temperature owing to surface combustion. The temperature, however, was liable to rise dangerously high if the hydrogen were present in suitable quantity, and, as safety from explosion was indispensable, this method was abandoned. The same apparatus was then applied with a much lower current, and with the wires consequently at a much lower temperature, to make use of the increase in thermal conductivity of the gas due to the admixture of hydrogen. This arrangement was found to be unexpectedly sensitive, and the method was adopted for the desired purpose. As the instrument was primarily intended to measure the purity of the air, the name "katharometer" was given to it.

In its final form, the katharometer consisted of two small helices of thin platinum wire (about 0·001 inch diameter), enclosed each in one of two cells in a copper block. The arrangement will be readily understood from a reference to the accompanying figure (fig. 1). Each helix was mounted in a

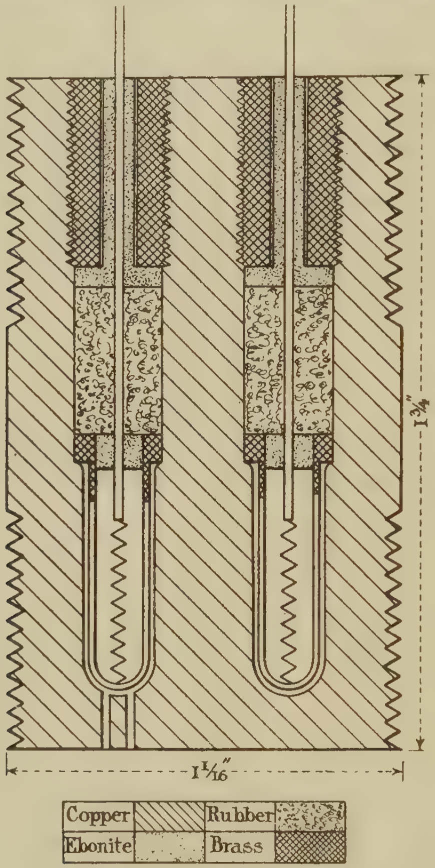

Fig. 1.—Diagram showing vertical section of the Katharometer.

small frame, consisting of a loop of copper wire soldered to a ring of copper. This ring was fitted with an insulating plug, through which the lead wire, also of copper, was introduced. One extremity of the helix was soldered to the lead and the other to the distal end of the loop. The outer part of the lead passed through a plug of rubber fitting into the cell, and over this rubber an ebonite plug was pressed down by a screw collar or nipple. Thus the rubber filled tightly the upper part of the cell, and access of air or gas could only take place by diffusion through the rubber. This diffusion is a slow process, and, for the purpose for which the katharometer was originally intended, such a joint was sufficiently nearly gas-tight. Minor improvements in detail were afterwards introduced. Both cells were similarly fitted, but whereas one was thus hermetically sealed, the other communicated with the outer atmosphere through three small holes. The resistance of each helix was about 8 ohms when cold, and the main working current in the bridge was usually 0·100 ampère; this was sufficient for most purposes, and gave the wires a temperature about 15° C. above that of the block. The remaining arms of the bridge were of manganin wire.

The instrument proved valuable for war purposes in various ways, *e.g.*, in testing the purity of hydrogen in balloons, testing the permeability of balloon and airship fabrics to hydrogen, testing permeability of sheets of metal, etc. Notes on some of these applications (which were confidential during the war) will no doubt be published in due course by the proper authorities.

The katharometer has already shown itself a valuable instrument for research, and is evidently capable of wide application.

Mr. H. A. Daynes, who was a research student under my charge, gave me valuable assistance throughout, and, at my request, developed the theory of the katharometer, as described in the following paper.]

The development of the katharometer as an instrument of precision demands some theory of its working to enable us to interpret its readings. For this purpose some description of the apparatus is necessary. The sensitive element is contained in a hole, 1·5 cm. long and 0·6 cm. in diameter, drilled in the copper block. Its volume is, therefore, about 0·5 c.c. The platinum helix is supported at the lower end on a frame of No. 22 S.W.G. wire rolled into a strip forming three sides of a rectangle and fitting fairly closely to the walls of the cell. The other end is soldered to a copper lead, which enters through an ebonite plug at the upper end of the cell. The helix is wound from about 8 cm. of pure platinum wire, 0·001 inch thick, the diameter of the spiral being about 1 mm. The resistance is about 10 ohms. The length of the helix is about 8 mm.

The electrical arrangement is shown in fig. 2.

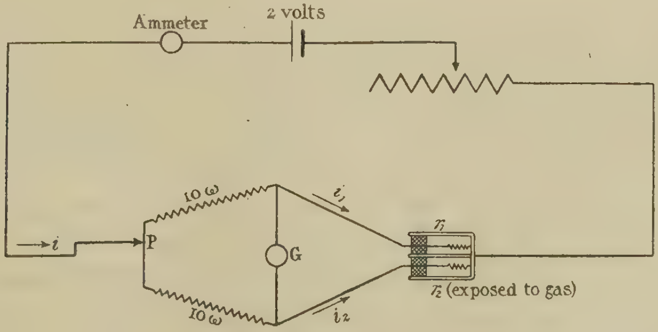

Fig. 2.

Two arms of the Wheatstone bridge are the platinum spirals (one exposed to the gas, whose composition is variable). The other arms of manganin are joined by a graduated bridge wire, and the point of contact (P) is always varied so that the galvanometer (G) gives zero reading. The current is always adjusted to a definite value, i.

Heat Losses in the Katharometer Cell.

The platinum wire is so thin that its temperature follows variations in the surrounding gas very quickly so we only have to consider steady conditions when the heat is carried away from the wire at the same rate as it is developed by the current in the wire.

Radiation is negligible. If we take Lummer and Kurlbaum's value for the radiation for polished platinum

$$e = 0{\cdot}514\left(\frac{\theta}{1000}\right)^{5\cdot2}$$

where e is the energy per second in watts, radiated per square centimetre, and θ is the temperature of the wire, it can be shown that at the highest temperatures used in the katharometer, the radiation loss is approximately 0·1 per cent. of the total heat loss and is, of course, relatively less at lower temperatures.

The relative importance of convection and conduction is very difficult to estimate. The cell was made small in order to increase conduction losses and decrease convection losses as far as possible. This is of practical importance in making the readings independent of changes of pressure. The obstructions to circulation of the gas must also tend to reduce convection considerably The circulation will cause least disturbance in the neighbourhood of the wire where the temperature gradients are steep and so only operate when they can have little effect on the heat loss from the wire. As evidence of the smallness of the convection effects it can be stated that the heat loss only increases 0·004 per cent. for a rise in pressure of 1 cm. of mercury. Also very little change of zero takes place in tilting the katharometer into different positions and such change as there is may be due to the sagging of the wires.

It is not possible to calculate what would be the heat loss which would be accounted for by conductivity; there are too many complications introduced by the design of the cell.

It is, therefore, assumed throughout the following theory that the convection losses, if not negligible, are so similar in their action to conduction losses that they only modify the absolute value of the heat losses. So that when we speak of the conductivity of the gas in the cell we mean to include convection losses as well.

We, therefore, consider as a working hypothesis that the heat losses in the cell are proportional to the difference between the temperature of the wire and that of the copper block and also to the thermal "conductivity" of the gas in the cell. But the conductivity varies considerably with temperature so it is necessary to decide what to take as the mean thermal conductivity.

Let conductivity at temperature θ be $K_\theta = K_0(1+\beta\theta)$ where β is a constant over the range considered. In most simple cases it may be shown that, in the steady state, if θ_1 and θ_2 be the boundary temperatures of the medium, the mean conductivity

$$K_m = \frac{K_\theta + K_{\theta_1}}{2} = K_0\left(1+\beta\frac{\theta_1+\theta_2}{2}\right).$$

The simple case which most nearly approaches that of the katharometer is that of two co-axial cylinders at different temperatures and it can be shown that the above relation applies to this case. The comparison with two co-axial cylinders would be complete if: (1) the radius of the wire were so small compared with the distance between separate turns of the spiral and the radius of the chamber that the turns did not appreciably affect one another; or (2) in the opposite extreme, if the spiral were so closely wound that the heat might be considered as developed uniformly over a cylinder on which lies the helical axis of the wire.

The case of the katharometer is intermediate.

End Correction.

The effect of cooling of the end of the katharometer wire by the cool copper lead must next be considered. The copper lead is thick compared with the platinum wire and is exposed, at a very short distance from the connection, to the outside air, so we shall assume, to get a rough idea of the magnitude of the error, that both the copper block and the end of the platinum wire are at zero (room) temperature. We shall also neglect the variation in the resistance from point to point of the wire, in considering the heat produced by the current.

Consider a long thin platinum wire, radius a, of thermal conductivity K' and resistance per centimetre r. A current i is flowing through it. Let the temperature at a distance x from the end at zero temperature be θ.

In a small element of length Δx,

Heat produced per second by the current $= \dfrac{i^2 r\Delta x}{J}$

(J = mechanical equivalent of heat),

Heat lost from sides by conduction per second $= A\theta\,\Delta x$, Heat leaving the element by conduction along the wire to the cool part

$$= K'\pi a^2 \frac{d\theta}{dx}$$

Heat entering the element by conduction from the warm part

$$= K'\pi a^2 \frac{d}{dx}\left(\theta + \frac{d\theta}{dx}\,\Delta x\right),$$

$$\therefore \qquad \frac{i^2 r\,\Delta x}{J} + K'\pi a^2 \frac{d}{dx}\left(\theta + \frac{d\theta}{dx}\,\Delta x\right) = K'\pi a^2 \frac{d\theta}{dx} + A\theta\,\Delta x,$$

$$\therefore \qquad \frac{i^2 r}{J} + K'\pi a^2 \frac{d^2\theta}{dx^2} = A\theta,$$

or

$$\frac{d^2\theta}{dx^2} - \frac{A}{\pi a^2 K'}\,.\,\theta = -\frac{i^2 r}{J\pi a^2 K'}.$$

The solution which satisfies the conditions

$$x = 0, \qquad \theta = 0$$

and

$$x = \infty, \qquad \frac{d\theta}{dx} = 0,$$

is

$$\theta = \frac{i^2 r}{JA}\left(1 - e^{-x\sqrt{A/\pi a^2 K'}}\right).$$

If the katharometer wire is long enough for the centre not to be appreciably affected by end cooling, the resistance of a wire of length l, whose temperature coefficient of resistance is α,

$$= 2r_0 \int_0^{l/2} (1 + \alpha\theta)\,dx$$

$$= 2r_0 \int_0^{l/2} \left[1 + \alpha \left\{\frac{i^2 r}{JA}\left(1 - e^{-x\sqrt{A/\pi a^2 K'}}\right)\right\}\right] dx$$

$$= 2r_0 \left[l/2\left(1 + \alpha\frac{i^2 r}{JA}\right) - \alpha\,.\,\frac{i^2 r}{JA}\sqrt{\frac{\pi a^2 K'}{A}}\right].$$

Therefore, $$\frac{\text{effective temperature of wire}}{\text{temperature of middle of wire}} = \frac{l - 2\sqrt{\pi a^2 K'/A}}{l}$$

or the end correction is $\sqrt{\dfrac{\pi a^2 K'}{A}}$ cm. for each end.

To estimate this we may take the following experimental values for air

$$a = 1{\cdot}2 \times 10^{-3}\ \text{cm.}, \qquad K = 0{\cdot}16,$$

$$A = 1{\cdot}4 \times 10^{-4}\ \text{watts/cm.} = 3{\cdot}3 \times 10^{-5}\ \text{cals./cm. sec.}$$

$$\therefore \quad \sqrt{\frac{\pi a^2 K'}{A}} = 0{\cdot}15\ \text{cm. approximately.}$$

This end correction must therefore be taken into account and determined with a fair degree of accuracy if any results are to be drawn from experiments as to the thermal conductivity of a gas. It will be seen that the end correction varies inversely as the square root of the conductivity of the gas.

Summary of Previous Experimental Work.

In 1916 the writer carried out some experiments to test the assumptions stated here as to the nature of the heat losses from a katharometer wire. The way in which the temperature of a wire varied with rate of production of energy by the heating current was investigated. This was done with both air and hydrogen surrounding the wire. The results were such as to confirm the general conclusions reached in the discussion.

If i is the current in a katharometer helix of resistance r, a is a constant depending on the form of the helix, K_0 is the effective conductivity of the gas at 0° C., β is the temperature coefficient of conductivity of the gas, θ is the temperature of the copper block, and θ_1 the temperature of the hot wire, it was found that the relation was represented by an equation

$$i^2 r = aK_0\left(1+\beta\,\frac{\theta+\theta_1}{2}\right)(\theta_1-\theta).$$

The following values were found for a typical helix.

In air $aK_0 = 8{\cdot}35 \times 10^{-4}$ watts/1° C and $\beta = 0{\cdot}0030/1°$ C.,
and in hydrogen

$$aK_0 = 59{\cdot}5 \times 10^{-4} \text{ watts}/1^\circ \text{ C.} \quad \text{and} \quad \beta = 0{\cdot}0022/1^\circ \text{ C.}$$

This gives
$$\frac{K_0 \text{ for hydrogen}}{K_0 \text{ for air}} = 7{\cdot}12.$$

The results are not of high precision, but they are sufficiently accurate to justify us in using the above equation to develop the theory of the action of two katharometer coils when used in a bridge as described at the beginning of the paper.

Theory.

Under these conditions we have to take into account the fact that we do not measure the current through any one of the platinum coils, but the total current in the bridge, and the resistances of the katharometer coils.

It is proposed to find the ratio of the resistances of the two katharometer coils, as indicated by the balance point on the graduated bridge wire. This will be carried as far as terms of the second order of temperature coefficients since the whole effect observed is of the first order of the temperature coefficient of resistance of the platinum wire. To do this, we only need to determine the excess temperatures of the wires to the first order of temperature coefficients.

Notation.

θ = temperature of copper block.
i = current in battery circuit.
α = temperature coefficient of resistance of platinum.

In the first katharometer coil:

i_1 = current through coil.
θ_1 = temperature of coil.
r_1 = resistance of coil at temperature θ_1.
r_{10} = resistance of coil at temperature 0° C.
K_1 = conductivity of gas surrounding coil when the wire is at a temperature θ_1.
K_{10} = conductivity of gas at 0° C.
a_1 = constant depending on the shape of wire, etc.,
and β_1 = temperature coefficient of conductivity of gas surrounding the coil.

Similar letters with the suffix $_2$ refer to similar quantities in the second coil.

We shall find it convenient to denote the ratio $\frac{a_1K_{10}r_{10}}{a_2K_{20}r_{20}}$ by ϕ, a function inversely proportional to K_{20} when the gas is varied. We wish to take account of the three variables i, θ, K_2, when the first cell is used as a standard.

The experimental relations are,

$$i_1{}^2r_1 = a_1K_1(\theta_1-\theta) \qquad \text{where} \qquad r_1 = r_{10}(1+\alpha\theta_1)$$

$$\text{and} \qquad K_1 = K_{10}\left(1+\beta_1\frac{\theta+\theta_1}{2}\right),$$

and

$$i_2{}^2r^2 = a_2K_2(\theta_2-\theta) \qquad \text{where} \qquad r_2 = r_{20}(1+\alpha\theta_2)$$

$$\text{and} \qquad K_2 = K_{20}\left(1+\beta_2\frac{\theta+\theta_2}{2}\right),$$

$$\therefore\ \theta_1-\theta = \frac{i_1{}^2r_1}{a_1K_1} = i^2\left(\frac{r_2}{r_1+r_2}\right)^2\frac{r_1}{a_1K_1}$$

$$= i^2\frac{r_{20}{}^2(1+\alpha\theta_2)^2}{\{(r_{10}+r_{20})+\alpha(r_{10}\theta_1+r_{20}\theta_2)\}^2}\cdot\frac{r_{10}(1+\alpha\theta_1)}{a_1K_{10}\{1+\beta_1(\theta+\theta_1)/2\}}$$

$$= i^2b\left[1+2\alpha\theta_2+\alpha\theta_1-2\alpha\frac{r_{10}\theta_1+r_{20}\theta_2}{r_{10}+r_{20}}-\frac{\beta_1}{2}(\theta+\theta_1)\right],$$

to the necessary degree of approximation if $b = \left(\frac{r_{20}}{r_{10}+r_{20}}\right)^2\frac{r_{10}}{a_1K_{10}}$.

Similarly

$$\theta_2 - \theta = i^2 b\phi \left[1 + 2\alpha\theta_1 + \alpha\theta_2 - 2\alpha \frac{r_{10}\theta_1 + r_{20}\theta_2}{r_{10} + r_{20}} - \frac{\beta_2}{2}(\theta + \theta_2) \right]$$

since

$$\left(\frac{r_{10}}{r_{10} + r_{20}} \right)^2 \frac{r_{20}}{a_2 K_{20}} = b\phi.$$

On the right-hand side of these equations we may substitute

$$\theta_1 = \theta + bi^2 \qquad \text{and} \qquad \theta_2 = \theta + b\phi i^2.$$

Then $\theta_1 - \theta = bi^2 \left[1 + (\alpha - \beta_1)\,\theta + bi^2 \left\{ \alpha \frac{(2\phi - 1)\,r_{10} + r_{20}}{r_{10} + r_{20}} - \frac{\beta_1}{2} \right\} \right]$

and

$$\theta_2 - \theta = b\phi i^2 \left[1 + (\alpha - \beta_2)\,\theta + bi^2 \left\{ \alpha \frac{r_{10}\phi + r_{20}(2 - \phi)}{r_{10} + r_{20}} - \frac{\beta_2 \phi}{2} \right\} \right],$$

$$\therefore \qquad \theta_1 - \theta_2 = bi^2 \Big[(1 - \phi)(1 + \alpha\theta) - (\beta_1 - \phi\beta_2)\,\theta$$
$$+ bi^2 \left\{ \alpha \frac{(1 - \phi)^2 (r_{20} - r_{10})}{r_{10} + r_{20}} - (\beta_1 - \phi^2 \beta_2) \right\} \Big].$$

Now $\dfrac{r_1}{r_2} = \dfrac{r_{10}(1 + \alpha\theta_1)}{r_{20}(1 + \alpha\theta_2)} = \dfrac{r_{10}}{r_{20}} \{ 1 + \alpha(\theta_1 - \theta_2) - \alpha^2 \theta_2 (\theta_1 - \theta_2) \}$

$$= \frac{r_{10}}{r_{20}} \Big\{ 1 + \alpha b i^2 \Big[(1 - \phi)(1 + \alpha\theta) - (\beta_1 - \phi\beta_2)\,\theta$$
$$+ bi^2 \left\{ \alpha \frac{(1 - \phi)^2 (r_{20} - r_{10})}{r_{10} + r_{20}} - \frac{\beta_1 - \phi^2 \beta_2}{2} \right\} \Big] - \alpha^2 (\theta + b\phi i^2)\, bi^2 (1 - \phi) \Big\}$$
$$= \frac{r_{10}}{r_{20}} \Big[1 + \alpha b i^2 \Big\{ (1 - \phi) - (\beta_1 - \phi\beta_2)\,\theta$$
$$+ \alpha b i^2 (1 - \phi) \left(1 - 2 \frac{r_{10} + \phi r_{20}}{r_{10} + r_{20}} \right) - bi^2 \frac{(\beta_1 - \phi^2 \beta_2)}{2} \Big\} \Big]. \qquad (1)$$

Interpretation of Equation (1).

It will be seen that the product bi^2 is of the dimensions of a temperature and is the excess temperature which the first spiral would reach if both resistances and thermal conductivities kept the values they have at 0° C. This is usually not more than 50° C. Since α is 0·0038 per degree Centigrade and β_1 and β_2 usually of the order of 0·002 per degree Centigrade, $\alpha b i^2$ is roughly not more than 0·2 so that the products $(\alpha b i^2)^2$ and $\beta_1\, \alpha\, (bi^2)^2$ are of the order of 0·04 and 0·02 respectively. This will give some idea of the relative importance of the last two terms.

When the conductivity of one of the gases is changed, the main effect observed is represented by the term $\alpha b i^2 (1 - \phi)$. The sensitiveness, therefore, varies nearly as the square of the current if the bridge is always balanced.

But as the current is increased the potential fall across the bridge is increased in proportion, and the galvanometer is more sensitive to a given movement on the bridge wire. The real sensitiveness, therefore, varies nearly as the cube of the current.

Deviations from this law are represented by the other three terms of the expression given above. The second term $\alpha b i^2 (\beta_1 - \phi\beta_2)\theta$ represents the change of sensitiveness as the temperature of the katharometer changes. For small values of bi^2 if β_1 and β_2 are nearly the same the deflection has a temperature coefficient of $-\beta_1$, *i.e.*, the same as that of the conductivity of the gas but with the sign reversed.

The next term, $\alpha (bi^2)^2 (1-\phi) \left\{1 - 2\frac{r_{10} + \phi r_{20}}{r_{10} + r_{20}}\right\}$ represents the decrease in sensitiveness as the current rises, on account of the diversion of the current from the coil which is at the higher temperature to that which is at the lower temperature, thus tending to mask any difference in temperature between the two arms. The effect becomes more marked at higher currents.

The last term expresses the fact that, as the current is increased, the mean temperature of the gas round the higher temperature coil rises more rapidly than that round the other coil, so that the resulting difference of temperature between the two coils is less than if the conductivities were independent of temperature.

Both of the last two terms are usually opposed to the main effect.

We can now consider special cases. First consider the simple case where the two platinum coils are similar in resistance and shape, but the gas in the second chamber has a slightly different conductivity and not necessarily the same temperature coefficient of conductivity.

Let $\quad K_{20} = K_{10}(1+\epsilon), \qquad \therefore \quad \phi = 1-\epsilon.$

Equation (1) then becomes

$$\frac{r_1}{r_2} = \frac{r_{10}}{r_{20}}\left[1 + \alpha b i^2 \left\{\epsilon - (\beta_1 - \beta_2 + \beta_2\epsilon)\theta + \alpha b i^2 \epsilon \left(\frac{r_{20}\epsilon - r_{10}}{r_{10} + r_{20}}\right) - bi^2 \frac{\beta_1 - \beta_2 + 2\epsilon\beta_2}{2}\right\}\right]. \qquad (2)$$

Suppose the small change ϵ is produced by the admixture of a small percentage of another gas, and suppose over the range considered

$$\beta_2 = \beta_1(1+\delta).$$

Then

$$\frac{r_1}{r_2} = \frac{r_{10}}{r_{20}}\left[1 + \alpha b i^2 \left\{\epsilon - \beta_2(\epsilon - \delta)\theta + \alpha b i^2 \epsilon \left(\frac{r_{20}\epsilon - r_{10}}{r_{10} + r_{20}}\right) - bi^2 \left(\frac{\beta_2(2\epsilon - \delta)}{2}\right\}\right]. \qquad (3)$$

Application of the Theory.

If $\epsilon = 0$ and $\delta = 0$ the balance point is independent of current and temperature, as we might expect.

In measuring small changes of conductivity or composition of a mixture it is most desirable that the zero should be independent of changes of current and temperature. The main effect is eliminated if $\phi = 1$ (*i.e.*, $\epsilon = 0$), so in all cases where small changes are to be measured it is arranged, if possible, that $\phi = 1$. (The methods of effecting this will be discussed later, but we do not assume that β_1 and β_2 are necessarily equal.)

The variations of zero may be represented by the partial derivatives $\frac{\partial}{\partial\theta}\left(\frac{r_1}{r_2}\right)$ and $\frac{\partial}{\partial(i^2)}\left(\frac{r_1}{r_2}\right)$ substituting $\epsilon = 0$ and values for β_1 and β_2 suitable to $\epsilon = 0$ and the change of balance point for a given change of conductivity by $\frac{\partial}{\partial\epsilon}\left(\frac{r_1}{r_2}\right)$.

In the case of small percentages of gases in air this is simple since $\epsilon = 0$ and $\delta = 0$,

$$\therefore \qquad \frac{\partial}{\partial\theta}\left(\frac{r_1}{r_2}\right)_{\substack{\epsilon = 0\\ \delta = 0}} = 0, \qquad \frac{\partial}{\partial i^2}\left(\frac{r_1}{r_2}\right)_{\substack{\epsilon = 0\\ \delta = 0}} = 0,$$

and

$$\frac{\partial}{\partial\epsilon}\left(\frac{r_1}{r_2}\right) = \frac{r_{10}}{r_{20}}\left[\alpha b i^2\left\{1 - \beta_2\theta + \alpha b i^2\left(\frac{2 r_{20}\epsilon - r_{10}}{r_{10} + r_{20}}\right) - b i^2\beta_2\right\}\right]. \tag{4}$$

If the gas to be dealt with is considerably different from air, it is possible to keep the other coil of the katharometer surrounded by another gas whose conductivity is nearly that of the gas under investigation. The following are examples of pairs of mixtures of gases and pure gases which are very roughly equal in conductivity :—

Pure methane and 15 per cent. hydrogen in air.
Coal gas and 50 per cent. hydrogen in air.
Oxygen and 0·8 per cent. hydrogen in air.
Ammonia and 10 per cent. of either carbon-dioxide or nitrous oxide in air.

In this case we have again $\epsilon = 0$, but β_1 does not necessarily equal β_2 so formula (2) applies.

Then

$$\frac{\partial}{\partial\theta}\left(\frac{r_1}{r_2}\right)_{\epsilon = 0} = -\frac{r_{10}}{r_{20}}\,\alpha b i^2(\beta_1 - \beta_2), \tag{5}$$

$$\frac{\partial}{\partial i^2}\left(\frac{r_1}{r_2}\right)_{\epsilon = 0} = -\frac{r_{10}}{r_{20}}\,\alpha b(\beta_1 - \beta_2)(\theta + b i^2), \tag{6}$$

and

$$\frac{\partial}{\partial\epsilon}\left(\frac{r_1}{r_2}\right) = \frac{r_{10}}{r_{20}}\left[\alpha b i^2\left\{1 - \beta_2\theta + \alpha b i^2\,\frac{2 r_{20}\epsilon - r_{10}}{r_{10} + r_{20}} - b i^2\beta^2\right\}\right]. \tag{7}$$

These equations show that, although, in the case of two different gases, the zero depends to a small extent on the current and temperature, the change of balance point for a given change of conductivity is the same as if the two gases had the same temperature coefficients of conductivity, provided that the change is reckoned from the zero suitable to the temperature and current at which the reading is taken. (Because equations (4) and (7) are identical.)

There is still another way of making $\phi = 1$, and this one is important because it is the basis of the hydrogen purity meter. Suppose we have an ordinary katharometer, in which the coils are exactly similar and the excess temperature with both arms in air is about 50° C. If one of these coils is now exposed to pure hydrogen, its excess temperature falls to about 10° C. If now the current fell by 1 per cent., the temperature of the unexposed coil would fall by about 1 per cent. without much alteration in that of the exposed one. But the effect in the bridge would be the same as would be produced by the addition of about 5 per cent. of air to the hydrogen. A change of temperature would produce similar effects.

It is obvious, therefore, that it is impracticable to have a hydrogen purity meter reading to 0·01 per cent. of impurity, or a research instrument (as used in the measurement of the air permeability of indiarubber) reading to 0·001 per cent. of air, without elaborate arrangements for keeping the current and temperature constant. The difficulty is avoided by making the coil exposed to hydrogen (and its corresponding bridge coil) lower in resistance than the other. The greater part of the current then flows through this arm and raises its temperature, at the same time lowering the temperature of the other. The ratio of resistances is so chosen that the temperature of the one coil in air is practically the same as that of the exposed one in hydrogen. The variations of zero then nearly disappear. This equalisation of temperatures is the physical meaning of making $\phi = 1$. We have made $\frac{a_1 r_{10}}{a_2 r_{20}} = \frac{K_{20}}{K_{10}}$.

The equations (5), (6), and (7) apply equally to this case and show that there is a small residual change of zero with temperature, since hydrogen and air have not the same temperature coefficients of conductivity. This is eliminated in practice by inserting a small length of manganin wire in series with one of the katharometer coils, and it is found that the zero even then is, for all practical purposes, independent of changes of current.

Readings by Direct Galvanometer Deflection.

In many cases it is convenient to keep the point of contact on the bridge wire fixed and read the direct deflections on the galvanometer when a change of resistance occurs in one arm of the bridge. In this case the assumption we have made before that the current is shared between the katharometer coils inversely as their resistance is not strictly true, because some current flows across from one side to the other through the galvanometer and slightly alters the temperature of the platinum coils. Usually the current through the galvanometer is not more than 10^{-4} ampères, and as the total current is 10^{-1} ampères, the effect need only be taken into account in very accurate work.

Another point to be noticed is that, although in balanced bridge work the displacement of balance point has the same temperature coefficient as that of the conductivity of the pure gas, the direct deflection of the galvanometer in fixed bridge work does not vary in the same way. This is because the current through the galvanometer depends on all the resistances in the bridge, so that the increase of resistance in the platinum coils with increasing temperature of the block tends to give a greater current through the galvanometer for a given change of resistance in one arm.

Consider the arrangement shown in fig. 3. a and β are manganin arms of the bridge, and α and b are the platinum coils of the katharometer. The bridge is slightly out of balance, so that a current z flows through the galvanometer when the current through the battery is always adjusted to a constant value x. It can then be shown that

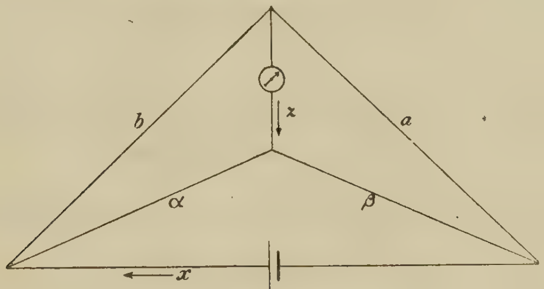

FIG. 3.

$$\frac{z}{x}=\frac{a\alpha-b\beta}{G(a+b+\alpha+\beta)+(b+\alpha)(a+\beta)}.$$

Let $\qquad b=k\alpha \qquad$ and $\qquad a=k(1+\epsilon)\beta$ where ϵ is small.

Then $\dfrac{z}{x}=\dfrac{k\alpha\beta\epsilon}{G(k+1)(\alpha+\beta)+\alpha\beta(k+1)^2}$ neglecting terms in $\beta\epsilon$ in comparison with α and β

$$=\frac{k\epsilon}{G(k+1)}\cdot\frac{1}{(1/\beta+1/\alpha)+(k+1)/G}.$$

If now a and β increase together in the same ratio, as they would in a katharometer for a given increase in room temperature if the gases had no temperature coefficient of conductivity,

$$\frac{\text{fractional change in } z/x}{\text{fractional change in } \beta} = \beta \cdot \frac{x}{z} \cdot \frac{d}{d\beta}\left(\frac{z}{x}\right)$$

$$= \frac{1}{(1+\beta/\alpha)+\beta(k+1)/G}.$$

In the simplest case, where $\alpha = \beta = G$ and $k = 1$, as we usually have in a katharometer, this ratio is $\frac{1}{4}$, *i.e.*, if the temperature coefficient of resistance of the platinum wire is 0·0038 per 1° C. we should expect the sensitiveness of the bridge to increase by about 0·10 per cent. per 1° C. rise in temperature. This would tend to reduce the expected fall of 0·30 per cent. in sensitiveness due to the increase in conductivity of the air and give us a final temperature coefficient of direct deflection of −0·20 per cent. per 1° C. This is in good agreement with an experimental value which gave −0·21 per 1° C. The magnitude of the effect varies, of course, with the bridge arrangement.

The Process of Diffusion through a Rubber Membrane.

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Introduction.

The production of balloon and airship fabrics in large quantities during the war has raised many problems in connection with leakage of hydrogen through membranes. It is desirable to have more information about the process by which gas passes through such rubber membranes.

In considering a rubber film, two alternatives have been suggested. One is that the chief obstacle to the passage of a gas is that provided by the material itself, and that the gas can pass the surfaces of the film quite readily. The other is that the chief obstacle is at the surface, the actual thickness of rubber having very little effect on the permeability.

The first view has been dealt with by Wroblewski (1) in 1879. He assumes:

(1) That when a piece of rubber is left exposed to a gas at normal pressure it absorbs a volume of gas which is a definite fraction of its own volume, and that this fraction, which he calls the "absorption coefficient," varies with the temperature of the rubber.

(2) That the absorption is proportional to the partial pressure of the gas.

(3) That when one side of a rubber membrane is exposed to hydrogen and the other to air, at a very short distance from the hydrogen surface, the concentration of gas in the rubber is the same as if the whole piece were immersed in hydrogen, and that a very short distance from the other face the concentration of hydrogen is negligible.

(4) That within the material Fick's Linear Diffusion Law holds as for free gases and liquids, *i.e.*, the nett rate of passage of gas in a given direction varies as the gradient of concentration of gas in that direction.

He therefore expresses the permeability of a fabric by a simple formula

$$Q = KA\frac{p_1-p_2}{l},$$

where Q = quantity passing through the fabric per second.
K = diffusion constant for the gas in the rubber.
A = absorption coefficient.
p_1 and p_2 = partial pressures of the permeating gas at the two sides of the fabric, either being unity when the gas is at normal pressure.
l = thickness of film.

The other view of the process is expressed in its extreme form in the statement that the permeability of a film is, within wide limits, independent of its thickness, *i.e.*, it can be expressed by a simple formula

$$Q = P(p_1-p_2).$$

It might be expected that each set of conditions would hold over extreme ranges of very thick and very thin films respectively, and that there would be an intermediate range of thickness where a formula would hold such as

$$Q = \frac{p_1-p_2}{R+l/KA},$$

where R may or may not be a constant for different values of l. If it were a constant the quantity RKA might be called the "equivalent extra thickness" of the surfaces.

The work done in this laboratory deals only with films from 0·03 to 1·6 mm. in thickness.

In considering evidence, a distinction has to be drawn between the case where a gas permeates through a membrane into a vacuum, and that where it permeates into another gas, because in the latter case there is a simultaneous absorption of the other gas. It remains to be shown to what extent the gases may be considered to act independently.

The following are results of absorption experiments by various workers.

Draper and Mitchell (2), about 1850, found that rubber absorbs about its own volume of carbon dioxide.

Wroblewski (3) in 1879 found the following values of the absorption coefficient A for rubber in strips at a temperature θ° C.:—

Nitrous oxide	$A_\theta = 1{\cdot}9561 - 0{\cdot}026649\,\theta$
Carbon dioxide	$A_\theta = 1{\cdot}2779 - 0{\cdot}015\,\theta$
Hydrogen	$A_\theta = 0{\cdot}02050 + 0{\cdot}004\theta$
Air	$A_\theta = 0{\cdot}06075 + 0{\cdot}0037\theta$

Hüfner (4), in 1888, using grey vulcanised rubber, found no absorption of air except that necessary for oxidation (5° C. to 25° C.), no nitrogen absorption (15° C. to 25° C.), no absorption of hydrogen (−2° C. to +13° C.), but rubber absorbed its own volume of carbon dioxide.

The only point on which these are agreed is that rubber absorbs its own volume of carbon dioxide.

In all these experiments the whole surface of the rubber was exposed to the gas. There is no question of the independence of action of two gases in a mixture. There is, also, no complication due to resistance at the surface. Experiments have, apparently, not yet been done on direct absorption of mixtures of gases. This would be of interest in connection with some permeability results to be described later.

It has been shown (5) that the absorption is proportional to the gas pressure.

When we come to consider the case of one gas diffusing through the membrane into another gas there is much more reliable evidence. The rubber used here was Para, with 5 per cent. litharge and about 3 per cent. sulphur.

1. (*a*) Under these conditions the quantity of hydrogen passing through is proportional to the partial pressure of the gas when one gas is pure air and the other a mixture of hydrogen and air (6) (7).

Also when two fabrics of permeabilities P_1 and P_2 are placed together in series and exposed on the two sides to hydrogen and air respectively, the permeability is $P_1P_2/(P_1+P_2)$ (8). This shows that the quantity passing through the fabric is proportional to the difference of partial pressure on the two sides when one gas is pure hydrogen.

Similar tests (9) with three fabrics in series test the case of mixtures on both sides.

(*b*) The temperature coefficient of permeability is, as nearly as could be measured, the same for all differences of partial pressure (10).

2. (*a*) The permeability of a rubber film is approximately inversely proportional to its thickness (11).

(*b*) The temperature coefficient of permeability is, over fairly wide ranges, independent of the thickness of the film (12).

3. (*a*) Work on the permeability of rubber films and rubbered fabrics to various gases (13) (14) shows no obvious correlation between permeability and density or molecular structure of the gas. The rates of passage of nitrogen and oxygen are very different, although they have nearly the same densities and molecular structure. Carbon dioxide and water vapour pass very freely.

(*b*) The temperature coefficient of permeability is not the same for all gases, nor is there any obvious relation between this and other physical constants of the gases (15).

4. With regard to the independence of action of several gases in a mixture:

(*a*) The permeability of rubber to carbon dioxide is the same within 2 per cent. whether hydrogen or air is on the other side of the fabric, over a range of 10° C. to 23° C. (16); and

(*b*) The total volume of gas passing through the rubber from nitrogen and oxygen in atmospheric proportions to hydrogen is the same within 2 per cent. over a range of 10° C. to 23° C. as if each gas acted independently according to its partial pressure (17).

It will be seen that all the results here quoted are consistent with the following assumptions:

(1) That Fick's diffusion law holds inside the material;

(2) That absorption of a gas is proportional to the partial pressure, independently of the presence of any other gases;

(3) That there is no appreciable resistance at the surface to the passage of the gas; and

(4) That the different gases present do not appreciably impede one another in passing through the rubber.

If one of these conditions did not hold, the others would have to be adjusted in some complicated way to account for the experimental results.

If these conditions do hold, we can then speak of a definite concentration of hydrogen at a given point in the rubber, and the problem of permeability in films and such membranes become calculables according to the same laws as diffusion of gases through one another.

This has suggested the experiments described later in this paper, in which the time taken to set up steady conditions of passage through a rubber film is used to separate out the parts played by diffusion and absorption of the gas in the whole process.

Theory of the Method.

Evidence has been given in the introduction that the problem of diffusion of hydrogen through rubber may be treated in the same way as the problem of diffusion through a similar space filled with gas.

We can therefore use the differential equation of diffusion

$$Q = -K\frac{dy}{dx},$$

where Q is the flux of hydrogen in the direction of x in c.c. per second,
K is the "diffusion constant" for hydrogen in the rubber,
y is the concentration of hydrogen at the point x in c.c. of hydrogen at N.T.P. per c.c. of rubber.

This equation is to be applied to each gas, independently of other gases present, using, of course, the appropriate value of K.

As boundary conditions we have at a surface where the partial pressure of hydrogen is p, $y = Ap$ where A is the absorption coefficient of hydrogen in rubber, *i.e.*, the saturation value of y for gas at normal pressure.

It is not possible to obtain from permeability experiments alone any idea of the separate values of K and A. For example, in the case of a uniform sheet of thickness l we have volume of gas passing through per second in the steady state,

$$Q = \frac{KAp}{l}.$$

Measurements of permeability only determine the product KA. But if we measure the time taken to set up a steady state we obtain some information as to the absolute values of K and A.

Consider a uniform film of thickness l. Initially, both faces are exposed to air. At a given instant one face is exposed to hydrogen. It is required to find the rate at which hydrogen is given off from the other face at any given time t.

The general solution for the case where

$$y = y_1 \text{ for } x = 0,$$

$$y = y_2 \text{ for } x = l,$$

and

$$y = f(x) \text{ at } t = 0 \text{ is (18)},$$

$$y = y_1 + (y_2 - y_1)\frac{x}{l} + \frac{2}{\pi}\sum_{n=1}^{n=\infty}\frac{y_2\cos n\pi - y_1}{n} \,.\, \sin\frac{n\pi}{l}x \,.\, e^{-Kn^2\pi^2t/l^2}$$

$$+\frac{2}{l}\sum_{n=1}^{n=\infty}\sin\frac{n\pi}{l}x e^{-Kn^2\pi^2t/l^2}\int_0^l f(x')\sin\frac{n\pi}{l}x'\,dx'.$$

In this special case

$$f(x) = 0, \qquad y_1 = 0, \qquad \text{and} \qquad y_2 = \mathrm{A}p.$$

Therefore, $y = \mathrm{A}p\dfrac{x}{l} + \dfrac{2}{\pi}\sum\limits_{n=1}^{n=\infty} \mathrm{A}p\,\dfrac{(-1)^n}{n} \,.\, \sin\dfrac{n\pi}{l}x \,.\, e^{-\mathrm{K}n^2\pi^2t/l^2}.$

Therefore,

$$\frac{dy}{dx} = \frac{\mathrm{A}p}{l} + \frac{2}{\pi}\sum_{n=1}^{n=\infty} \mathrm{A}p\,\frac{(-1)^n}{n} \,.\, \frac{n\pi}{l} \,.\, \cos\frac{n\pi}{l}x \,.\, e^{-\mathrm{K}n^2\pi^2t/l^2}.$$

At the face $x = 0$,

$$\underset{x\to 0}{lt}\left(\frac{dy}{dx}\right) = \frac{\mathrm{A}p}{l} + \frac{2}{\pi}\sum_{n=1}^{n=\infty} \mathrm{A}p\,\frac{(-1)^n}{n} \,.\, \frac{n\pi}{l} \,.\, e^{-\mathrm{K}n^2\pi^2t/l^2}.$$

Therefore volume of hydrogen emitted per second from this face

$$= \mathrm{K}\underset{x\to 0}{lt}\left(\frac{dy}{dx}\right) = \frac{\mathrm{KA}p}{l}\left[1 + 2\sum_{n=1}^{n=\infty}(-1)^n e^{-\mathrm{K}n^2\pi^2t/l^2}\right].$$

Let the hydrogen from a given area of this film be collected into a space such that

$$\frac{\text{the volume of the space}}{\text{area of film}} = \mathrm{V}\text{ cm.},$$

i.e., the "effective depth" of the space is V cm. If this space contains no hydrogen initially and there is no leak from it, the concentration z of hydrogen in it will begin to increase steadily and we shall have

$$\mathrm{V}\frac{dz}{dt} = \frac{\mathrm{KA}p}{l}\left[1 + 2\sum_{n=1}^{n=\infty}(-1)^n e^{-\mathrm{K}n^2\pi^2t/l^2}\right].$$

Integrate this and put in the condition that $z = 0$ when $t = 0$ and we have

$$z = \frac{\mathrm{KA}p}{\mathrm{V}l}\left[t + 2\sum_{n=1}^{n=\infty}\frac{(-1)^n}{n^2} \,.\, \frac{l^2}{\mathrm{K}\pi^2}(1 - e^{-\mathrm{K}n^2\pi^2t/l^2})\right].$$

As t increases indefinitely the graph of y approximates to the line

$$z = \frac{\mathrm{KA}p}{\mathrm{V}l}\left[t + 2\frac{l^2}{\mathrm{K}\pi^2}\sum_{n=1}^{n=\infty}\frac{(-1)^n}{n^2}\right].$$

But

$$\sum_{n=1}^{n=\infty}\frac{(-1)^n}{n^2} = -\frac{\pi^2}{12}.$$

Therefore the final line is

$$z = \frac{\mathrm{KA}p}{\mathrm{V}l}\left[t - \frac{l^2}{6\mathrm{K}}\right].$$

This line cuts the axis $0t$ at a time $l^2/6\mathrm{K}$ from the time when one face is exposed to hydrogen. We shall call this time the "lag." The quantity per second emitted in the steady state we shall call the permeability.

Then permeability, $P = \frac{KAp}{l}$; lag, $L = \frac{l^2}{6K}$,

and we have

$$PL = \frac{pl}{6}A.$$

We have, then, a means of determining both the absorption coefficient A and the "diffusion constant" K.

Description of Apparatus.

The apparatus used was a modification of the Shakespear permeability tester (19) (fig. 1). This consists essentially of—

(1) An air chamber of known volume, having a flange on which the material to be tested is placed;

(2) A hydrogen chamber, having a flange which, together with the flange on the air chamber, grips the test piece; and

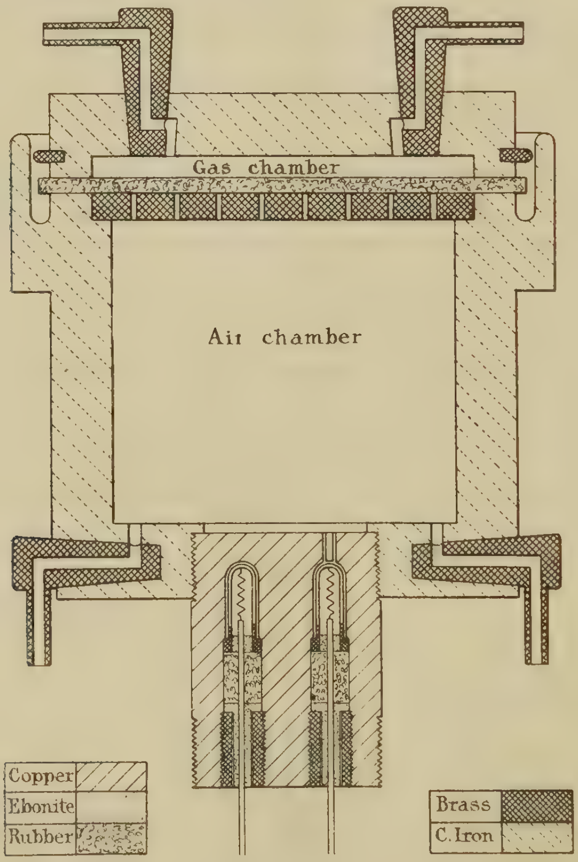

Fig. 1.—Vertical Section of Permeameter.

(3) A katharometer, *i.e.*, a direct reading instrument, which indicates the composition of a mixture of hydrogen and air at any given instant.

In these experiments, films were used such that the test area was a circle of 2·225 cm. diameter. The air chamber was a cylindrical vessel of cast iron, having a cylindrical hole in it about 4 cm. deep and 4 cm. in diameter. From the top it was shouldered out to a depth of about 4 mm., and on the shoulder rested a grid of brass strips, placed with their edges up, and having a square mesh of about 3 mm. side. The top of this grid was then turned flush with the top flange. This arrangement served to keep the fabric from sagging. Inlet and outlet taps opened into the bottom of this cavity.

The film was then laid on the flange and sealed. The hydrogen chamber was a cylindrical vessel of internal diameter equal to that of the top of the air chamber. It was only about 4 mm. deep. The open end was turned to rest on the flange of the air chamber, the whole lid being centred by a rim turned on the air chamber. Hydrogen could be introduced through taps which could be turned on or off by rotating the tubes through a right angle.

The katharometer was screwed into the bottom of the air chamber. It consists of a copper block containing two cylindrical holes. Into each of these holes is placed, co-axially with the hole, a platinum helix. The two helices are similar, and form two arms of a Wheatstone bridge, the other two arms being of manganin. The current in the bridge heats both helices equally, so that they are kept at a temperature 30° C. or 40° C. above the temperature of the copper block. One hole is sealed up, and the other communicates with the air chamber through small holes drilled through the end of the cell containing the helix. The bridge is adjusted to give no current through the galvanometer when both helices are in dry air. When hydrogen is admitted to one chamber, the helix in that chamber is cooled, and the resulting change in its resistance causes a deflexion of the galvanometer. In these experiments a sensitive moving coil galvanometer was used with lamp and scale, giving a sensitiveness of about 1000 divisions to 1 per cent. hydrogen in air. It was possible, therefore, to estimate, by subdivision by eye, to about one part of hydrogen in 500,000 of air.

The instrument is very quick reading. It has a time-constant of about 15 seconds.

The volume of the air chamber was measured by filling it with water and weighing the water used.

The katharometer was calibrated directly in divisions, per 1 per cent. hydrogen, by passing into it definite mixtures of hydrogen and air.

Method of Testing.

It was shown earlier in the paper that, to obtain values of K and A, we have to measure both the permeability and the lag. When hydrogen is admitted to the hydrogen chamber, and the concentration of hydrogen measured in the air chamber and plotted against time, the curve is of the form shown in fig. 2.

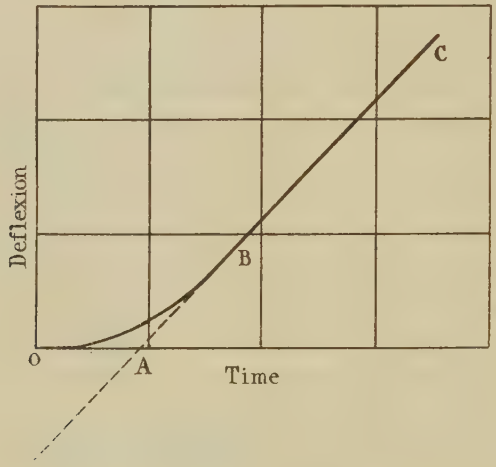

Fig. 2.—Typical Time—Deflexion Curve.

The slope of the final line BC gives us the permeability of the film, and the time represented by the distance OA is the lag.

It is necessary to consider what is the effect of the lag of the katharometer. Let v be the volume of the katharometer chamber, and let the communication holes be such that when there is a unit difference of concentration of hydrogen between inside and outside of the katharometer, q c.c. of hydrogen will escape per second.

Let $$\frac{q}{v} = b.$$

Then, if the katharometer initially has hydrogen at a concentration z_0, and is then exposed to air, the concentration in it, at time t, will be

$$z = z_0 \, e^{-bt},$$

$1/b$ is called the "time constant" of the katharometer, and is the time in which the concentration will fall to $1/e$th of its initial value.

It has been shown by the writer, in a previous note on the theory of the Shakespear permeameter (20), that if the hydrogen is continuously carried away from the air chamber, while a steady state is reached in the film, and then the air stream is suddenly stopped and the air chamber sealed, the indications of the katharometer vary with time according to the equation

$$z = \frac{P}{V}t - \frac{P}{Vb}(1-e^{-bt}),$$

where P = permeability of fabric,

$$V = \text{ratio } \frac{\text{volume of air chamber}}{\text{area of fabric}},$$

i.e., the time graph of z approximates after a time to the line

$$z = P/V(t-1/b),$$

which cuts the horizontal axis at a distance $1/b$ from the origin. This gives a very convenient way of measuring $1/b$.

The case of unsteady conditions, which we are considering, is more complicated.

The volume of the katharometer is small compared with that of the air chamber, so we have to find the concentration, ω, in the katharometer at any time, t, when the katharometer is exposed to a mixture whose concentration is varying according to the equation obtained in the first part of the paper, *i.e.*,

$$z = \frac{KAp}{Vl}\left[t + 2\sum_{n=1}^{n=\infty}\frac{(-1)^n}{n^2}\cdot\frac{l^2}{K\pi^2}(1-e^{-Kn^2\pi^2 t/l^2})\right].$$

For convenience of manipulation put

$$2\sum_{n=1}^{n=\infty}\frac{(-1)^n}{n^2}\cdot\frac{l^2}{K\pi^2} = a,$$

and

$$2\sum_{n=1}^{n=\infty}\frac{(-1)^n}{n^2}\cdot\frac{l^2}{K\pi^2}\cdot e^{-Kn^2\pi^2 t/l^2} = f(t),$$

and remember that

$$\underset{t\to 0}{lt}\, f(t) = a \quad\text{and}\quad \underset{t\to\infty}{lt}\, f(t) = 0.$$

Therefore

$$z = \frac{P}{V}[t+a-f(t)].$$

Then we have

$$\frac{d\omega}{dt} = \frac{q}{v}(z-\omega) = b\left[\frac{P}{V}\{t+a-f(t)\}-\omega\right].$$

Therefore

$$\frac{d}{dt}(\omega e^{bt}) = \frac{P}{V}\, b \,.\, e^{bt}[t+a-f(t)].$$

Therefore

$$\omega e^{bt} + B = b\,.\,\frac{P}{V}\left[\int te^{bt}\,dt + \int ae^{bt}\,dt - \int e^{bt}f(t)\,dt\right].$$

But
$$\int te^{bt}\,dt = \frac{1}{b}\cdot e^{bt}\left(t-\frac{1}{b}\right),$$

$$\int ae^{bt}\,dt = \frac{a}{b}e^{bt}$$

and
$$\int e^{bt}f(t)\,dt = 2\int\sum_{n=1}^{n=\infty}\frac{(-1)^n}{n^2}\cdot\frac{l^2}{K\pi^2}\cdot e^{(b-Kn^2\pi^2t/l^2)}$$

$$= 2\sum_{n=1}^{n=\infty}\frac{(-1)^n}{n^2}\cdot\frac{l^2}{K\pi^2}\cdot\frac{e^{(b-Kn^2\pi^2t/l^2)}}{b-Kn^2\pi^2/l^2}.$$

Therefore
$$\omega e^{bt}+B = \frac{P}{V}\left[e^{bt}\left(t-\frac{1}{b}\right)+ae^{bt}+2b\sum_{n=1}^{n=\infty}\frac{(-1)^n}{n^2}\frac{l^2}{K\pi^2}\frac{e^{(b-Kn^2\pi^2t/l^2)}}{b-Kn^2\pi^2/l^2}\right].$$

When
$$t = 0, \qquad \omega = 0.$$

Therefore
$$B = \frac{P}{V}\left[-\frac{1}{b}+a+2b\sum_{n=1}^{n=\infty}\frac{(-1)^n}{n^2}\cdot\frac{l^2}{K\pi^2}\cdot\frac{1}{b-Kn^2\pi^2/l^2}\right].$$

and therefore
$$\omega = \frac{P}{V}\left[t-\frac{1}{b}(1-e^{-bt})+a(1-e^{-bt})+2b\sum_{n=1}^{n=\infty}\frac{(-1)^n}{n^2}\cdot\frac{l^2}{K\pi^2}\frac{e^{-Kn^2\pi^2t/l^2}-e^{-bt}}{b-Kn^2\pi^2/l^2}\right].$$

After a time this approximates to
$$\omega = \frac{P}{V}\left[t-\frac{1}{b}+a\right].$$

The katharometer therefore increases the lag by its own time constant, and this quantity can be measured directly by a control experiment, which is simply the permeability test when a steady state is reached.

What has here been called the lag of the katharometer includes also the lag of galvanometer and lag introduced by diffusion of hydrogen from top to bottom of the air chamber. (This is probably of the order of 2 seconds.)

The difference between the lag in the unsteady state and that in the steady state is the lag due to absorption in the rubber + the lag due to flushing the hydrogen chamber.

Lag due to Flushing of Hydrogen Chamber.

To secure uniformity of flushing with hydrogen, side tubes led off from the inlet and outlet taps of the hydrogen chamber to the two arms of a differential manometer. The rate of flow was adjusted so that the manometer indicated a difference of pressure 1 cm. of water. To ensure this rate of flow from the instant of opening the taps, the outlet led to a glass tube, or "safety bubbler," dipping just under water and from a T-piece against the inlet a side tube led to another glass tube dipping 1 cm. under water. The following procedure was then adopted. With the inlet tap of the hydrogen chamber closed the rubber tube was detached from it and the hydrogen was allowed to run freely out at this opening so as to fill all the tubes with hydrogen right up to the tap. The rubber tube was then replaced and hydrogen then bubbled freely at the "safety bubbler" until the tap of the hydrogen chamber was turned on, when the required steady flow was established very quickly. Readings of the galvanometer were then taken every ¼ minute and plotted against time. Before the test dry air was passed above and below the film to secure drying of the rubber.

After this test a control experiment was done. The mixture at the bottom was flushed out with dry air while hydrogen was still running in the hydrogen chamber. The taps of the air chamber were then turned off at a given instant and readings again taken every quarter of a minute. The lag in this case is that of the katharometer and galvanometer and must be subtracted from the other lag to obtain that due to the absorption by the rubber and that due to flushing.

It was found that with a difference of 1 cm. of water between inlet and outlet the rate of flow of hydrogen was 4·1 c.c. per second. Since the volume of the hydrogen chamber was about 4 c.c. the lag introduced by flushing at this rate would be about 1 second. This was checked by a series of measurements of the lag in the case of a fabric when the difference of pressure between inlet and outlet was varied from 2 mm. to 18 mm. There was no difference in lag of more than 3 seconds between the extreme cases. In all calculations, therefore, 1 second is allowed for lag of flushing.

Seal between Film and Flange.

The making of a gastight seal between the film and the flanges of the permeameter presented some difficulty. At first the method which had proved successful with balloon fabrics was tried, *i.e.*, to dip the edges of the rubber in hot beeswax and vaseline up to a definite circle determined by two flat discs of iron which gripped the film. This proved unsatisfactory for two reasons:—

(1) The hot mixture caused the rubber to crinkle round the edge since there was no cotton to reinforce it; the hot mixture was also liable to alter the condition of the rubber round the edge.

(2) Too much pressure was required to press the flanges down tightly and make a gastight joint. By this pressure the film was considerably distorted.

The following methods also proved unsatisfactory :—

(*a*) Dry flanges with slight pressure.

(*b*) Vaselined flanges; vaseline spoils rubber much faster than beeswax and vaseline mixture.

(*c*) Glycerine; this made a good seal with very little pressure but the rubber film showed a tendency to slide about very easily. The glycerine also spread along the film and filled up the angles of the grid.

It was found more satisfactory to use a rubber-vaseline tap-grease with a high percentage of vaseline; 1 kgrm. load was sufficient. The grease did not tend to spread and there was very little slipping of the film. The area of specimen exposed was, therefore, that of the inside of the flange.

By a separate experiment it was found that the seal did not produce any effect on the film which would affect very seriously the permeability during the time of the test.

Results.

The experiments carried out up to the present time are by no means complete or representative of the final precision of the method. No complete series of films was available and during the work minor faults appeared in the apparatus which could not be remedied before the work was postponed in favour of more direct war research. The results as they stand are, however, of interest and it is hoped to carry out more complete work later.

We have to thank Mr. A. D. Ritchie, of Kingsnorth Naval Air Station, for supplying us with the films used in this investigation. Little is known about the rubber. All three films were vulcanised (probably cold-cured) and were made from pure Para rubber. They may have been made from separate samples so that their physical properties will probably not be directly comparable. Three films were used as shown in the following Table :—

Film.	Thickness in mm.	Surface density in grm./metre^2.	Correction factor for edge-effect.
R (*a*)	1·421	1328	1·07
R (*b*)	0·657	614	1·035
R (*c*)	0·328	280	1·015

In calculating the permeability of the films from the observed rate of rise of concentration, we have to allow for the fact that the thickness of the film is appreciable when compared with the radius of the specimen. In the absence of any exact estimate of the disturbance in the lines of flow at the edge of the specimen it is assumed that the effective addition to the radius is not less than zero and not more than the thickness of the film. Half the thickness of the film is added to the radius in all cases so as to give an approximation. Taking the radius of the specimen as approximately 20 mm. we have the correcting factor F for edge effect as given in the above Table.

In calculating the constant of the permeameter we use the following data :—

Volume of permeameter	50·1 c.c.
Area of film	15·55 cm^2.
Sensitiveness of katharometer ...	905 div. to 1 per cent. hydrogen in air at 20° C.

$$\text{Therefore 1 div. per min.} = \frac{50\cdot1}{100\times905\times15\cdot55\times60}\ \text{c.c./cm.}^2\ \text{sec.}$$

$$= 5\cdot94\times10^{-7}\ \text{cm./sec.,}$$

i.e., we multiply div. per min, by $5\cdot94\times10^{-7}$ to get permeability in cm./sec.

Two other corrections have to be applied for temperature.

(*a*) The katharometer decreases in sensitiveness by 0·002 per 1° C. rise in temperature. To reduce all results to 20° C., div./min. are multiplied by $1+0\cdot002(\theta-20)$.

(*b*) The permeameter measures volumes of hydrogen in cubic centimentres at the temperature of the experiment. For convenience all results are compared at 20° C., so in calculating permeabilities, div./min. are divided by $1+0\cdot0037(\theta-20)$.

The combination of these two corrections is to divide div./min. by $1+0\cdot0017(\theta-20)$.

The following Table shows results of tests on the three films described and includes rate of movement of galvanometer, lag after subtracting lag of control experiment and 1 second for flushing the hydrogen chamber, and temperature of test :—

Film.	Div./min.	Temperature.	Lag.	Permeability.	
		° C.			
R (*a*)	4·49 5·04 5·76	16·1 19·5 22·8	319 293 260	$2\cdot51\times10^{-6}$ $2\cdot80\times10^{-6}$ $3\cdot18\times10^{-6}$	Constant $\dfrac{5\cdot94\times10^{-7}}{1\cdot07\,(1+0\cdot0017\theta-20)}$ Thickness = 1·421 mm.
R (*b*)	9·11	16·3	76 (69)	$5\cdot20\times10^{-6}$ $(5\cdot90\times10^{-6})$	Constant $\dfrac{5\cdot94\times10^{-7}}{1\cdot033\,(1+0\cdot0017\theta-20)}$ Thickness = 0·657 mm.
R (*c*)	21·0 21·1 23·2	19·1 19·4 21·2	14 16 10	$12\cdot27\times10^{-6}$ $12\cdot32\times10^{-6}$ $13\cdot51\times10^{-6}$	Constant $\dfrac{5\cdot94\times10^{-7}}{1\cdot015\,(1+0\cdot0017\theta-20)}$ Thickness = 0·328 mm.

P, L, and PL are plotted against θ for R (a) in graphs I, II, and III respectively (fig. 3).

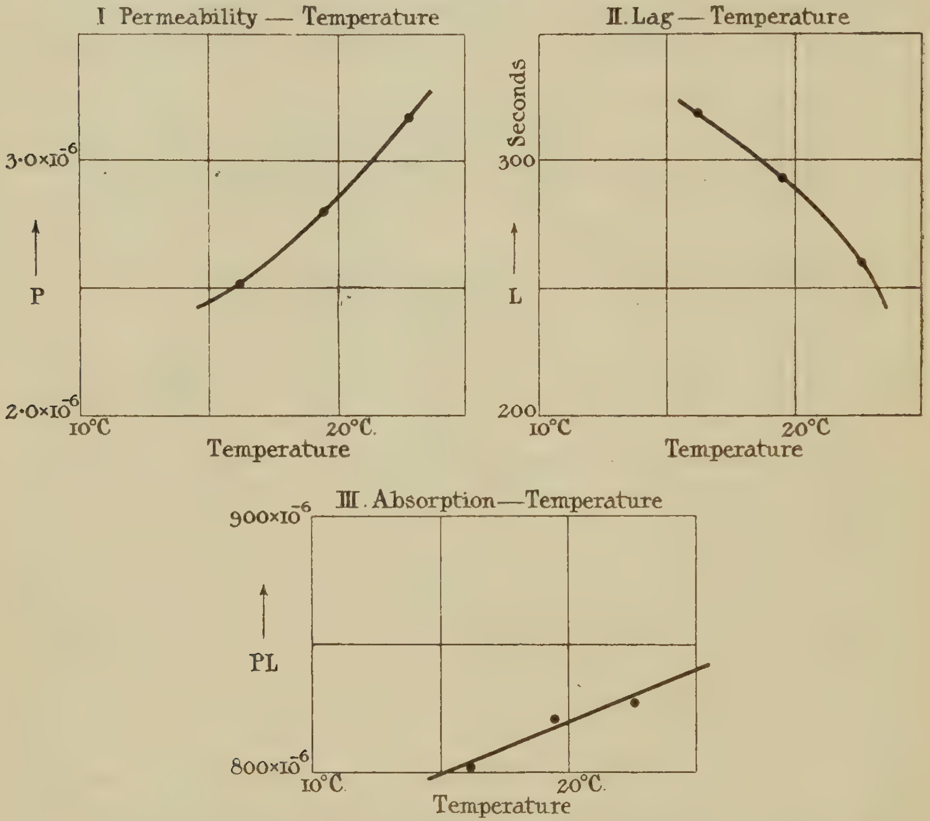

Fig. 3.—Relations between Permeability, Lag, and Temperature of Film.

The figures for P and L in brackets are those estimated for a temperature of 20° C., using the temperature curves of P and L for R (a) to obtain the correction.

Now, if the principles stated at the beginning of the paper hold, and if the rubbers in the different films are physically similar, we should expect the following relations to hold between permeability, lag, and permeability × lag, on the one hand, and thickness on the other :—

$$Pl = KAp, \qquad \frac{L}{l^2} = \frac{1}{6K}, \qquad \frac{PL}{l} = \frac{pA}{6},$$

all the quantities on the right-hand side being independent of l, the thickness of the film.

In the following table data are given for a temperature of 20° C., to enable these relations to be tested :—

Film.	l.	l^2.	P.	$\frac{1}{\mathrm{P}}$	L.
	cm.	cm².			secs.
R (a)	0·1421	$2·02 \times 10^{-2}$	$2·85 \times 10^{-6}$	$0·351 \times 10^{6}$	287
R (b)	0·0657	$0·432 \times 10^{-2}$	$5·90 \times 10^{-6}$	$0·169 \times 10^{6}$	69
R (c)	0·0328	$0·108 \times 10^{-2}$	$12·8 \times 10^{-6}$	$0·0782 \times 10^{6}$	13·3

	PL.	Pl.	$\frac{\mathrm{L}}{l^2}$	$\frac{\mathrm{PL}}{l}$
R (a)	818×10^{-6}	$0·405 \times 10^{-6}$	14,200	5760×10^{-6}
R (b)	407×10^{-6}	$0·388 \times 10^{-6}$	16,000	6200×10^{-6}
R (c)	170×10^{-6}	$0·420 \times 10^{-6}$	12,300	5180×10^{-6}

The quantities 1/P, L, and PL are plotted against l, l^2, and l respectively, in graphs IV, VI, and VII (fig. 4).

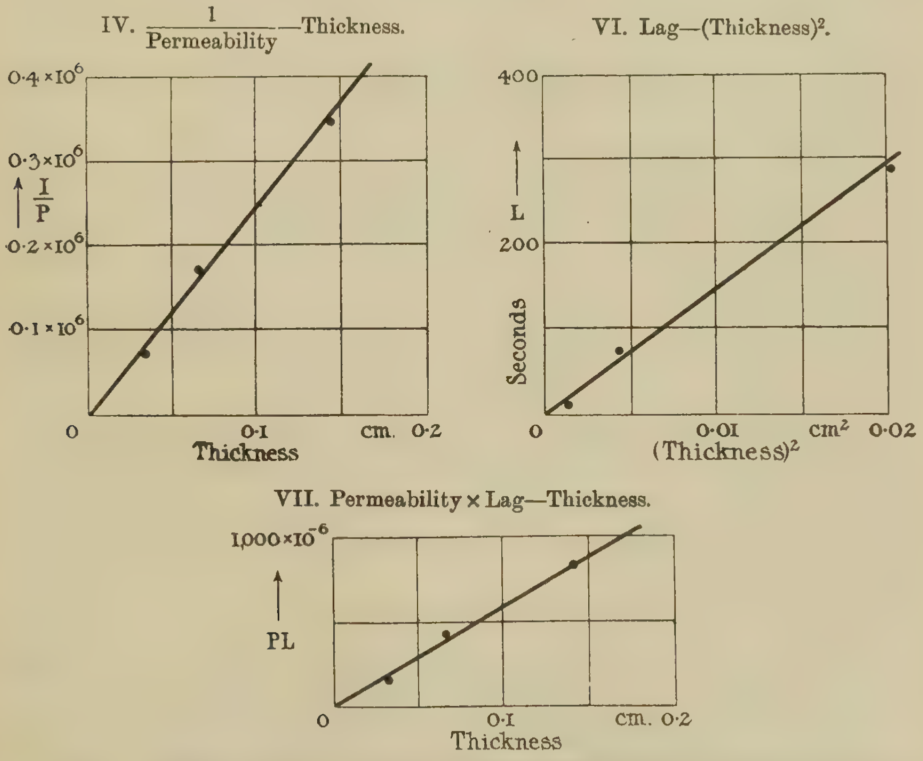

FIG. 4.—Relations between Permeability, Lag, and Thickness of Film at 20° C.

It will be seen from the Table that the quantities Pl, L/l^2 and PL/l, though different for different films, show no regular variation with l.

From the graphs V, VI, and VII slopes of lines give mean values as follows:—

$$\frac{L}{l^2} = 1{\cdot}46 \times 10^4, \quad \text{Therefore } K = \frac{1}{6 \times 1{\cdot}46 \times 10^4} = 11{\cdot}4 \times 10^{-6}\ \text{cm}^2/\text{sec.},$$

$$\frac{PL}{l} = 5{\cdot}3 \times 10^{-3} \qquad \text{and } A = \frac{6\,PL}{l} = 3{\cdot}5 \times 10^{-2}.$$

Graph III shows PL plotted against temperature, to show how the absorption coefficient depends on temperature. This shows a temperature coefficient at 20° C. of +0·5 per cent./1° C.

Conclusions.

1. The behaviour of the set of rubber films agrees in all respects, within the limits of error of the experiments, with that predicted from certain assumptions of a simple process of diffusion through a rubber membrane. The conclusion previously reached, that the surface resistance is negligible, is confirmed.

2. The method gives a quick and satisfactory means of measuring the absorption and diffusion-constant of a material for a gas, and is capable of development with greater precision.

3. The mean value for the diffusion-constant for the three films considered was $11{\cdot}4 \times 10^{-6}$ cm.-sec. at 20° C. The actual values for the three films separately were $11{\cdot}7 \times 10^{-6}$, $10{\cdot}4 \times 10^{-6}$, and $13{\cdot}6 \times 10^{-6}$ cm.-sec. (The last value is not so precise as the others.)

4. The mean value of the absorption coefficient was 0·035 at normal pressure and 20° C. The actual values for the three films were 0·035, 0·037, and 0·031. (The last value is not so precise as the others.)

5. The coefficient of absorption has a low temperature coefficient (approximately 0·5 per cent./1° C.), compared with that of the diffusion constant. It is not that which is responsible for the great variation of permeability with temperature. This suggests that the process of absorption is a simple molecular action.

Passage of other Gases through Rubber.

The method used for hydrogen has been applied to the study of hydrogen, nitrogen, oxygen, carbon dioxide, nitrous oxide, and ammonia.

The film used for these gases was in all cases about 0·4 mm. thick and all the films were cut from the same sheet.

In every case the time taken to reach a steady state was longer than for hydrogen, so the length of each test and the intervals between tests were necessarily longer. Not many tests, therefore, could be made on any particular film, as the permeability changed appreciably through edge effect of the sealing mixture within a single day. Good temperature curves were impossible, and in some cases it was impracticable even to make confirmatory tests. For the same reason, all the gases could not be tested on the same film, but of each film a test was taken with hydrogen, as a means of reference from one film to another. All tests were made at 17° C., as nearly as possible.

Special difficulties were met with oxygen, nitrogen, and ammonia.

The katharometer is not very sensitive to oxygen or nitrogen in air, so a special katharometer was used to show small traces of these gases in hydrogen. Hydrogen was then used instead of air as the gas into which the oxygen or nitrogen permeated. With this arrangement, the " natural leak " of the permeameter becomes very much more important. It was found that this leak was of the same order as the leak of air to be observed. To determine this leak as accurately as possible, readings were taken first with hydrogen flowing above and below the film. An approximately steady deflection was soon produced. The bottom chamber was then closed by the taps and the readings continued. The slope of the line, when readings were plotted against time, gave the natural leak of the permeameter. After this had continued sufficiently to determine the slope, the top chamber was flushed out with the gas to be examined by the same method as was used for hydrogen. The increase in the rate of movement of the galvanometer showed the extra leakage through the rubber. In measuring the lag it was necessary to note the point of intersection of the final line with the initial line with the original line (which showed the natural leakage) produced, not with the horizontal line through the reading at the time of introduction of the oxygen or nitrogen. A considerable part of the natural leak was probably due to the emission of absorbed air and water in the permeameter and film, and this emission was not constant. This greatly increased the difficulty of accurate measurement. It was not possible to dry out for a sufficient time to eliminate the effect, because of the edge deterioration of the rubber. The results on nitrogen, oxygen, and air are, therefore, of a much lower order of precision than the others. In fact, the leakage of nitrogen alone was not detectable, but those of oxygen and air were measurable. (Oxygen diffuses through rubber about twice as rapidly as nitrogen.)

The special difficulties with ammonia were due to:—

1. The low sensitiveness of the katharometer to ammonia;
2. The peculiar shape of the calibration curve of the katharometer for ammonia in air; and
3. The great length of time taken by the test.

The deflection for 1 per cent. of ammonia is only about one-tenth of that for 1 per cent. of hydrogen. It is in the same direction for small percentages but reaches a maximum, then zero, and finally at 100 per cent. ammonia a deflection in the opposite direction. The permeability to the gas is very high, so that in two hours there is a large percentage of ammonia in the bottom of the permeameter, and the curvature due to the calibration curve becomes very marked and back diffusion is considerable. But, by this time, steady conditions are not nearly reached, so there is no final straight line to produce back to cut the horizontal axis. Corrections have been applied so far as possible, and the given estimate of the lag is probably correct within 10 per cent.

The lag of the katharometer is due to the slowness of diffusion through the holes leading to the sensitive helix. It depends on the diffusion-constant of the gas, so separate control experiments had to be made with each gas.

The katharometer had also to be calibrated with each gas used by passing through it mixtures of known composition.

The results obtained are shown in the following Table. Where two or three confirmatory tests could be made the figure given is the mean of them :—

Film.	Thickness.	Gas.	Temperature.	Rate of galvanometer movement.	Total lag.	Katharometer lag.	Rubber lag.	Deflection per 1 per cent. of gas.
	cm.		° C.	div./min.	secs.	secs.	secs.	
[1]	$4 \cdot 29 \times 10^{-2}$	H_2	17·3	11·7	65	29·5	35·5	1001
		CO_2	17·6	4·17	495	134	361	−132
[2]	$4 \cdot 12 \times 10^{-2}$	H_2	16·0	11·8	73	31	42	1001
		N_2O	17·0	7·3	516	120	396	−134
		H_2	16·6	11·8	73	31	42	1001
[3]	$4 \cdot 55 \times 10^{-2}$	Air	17·2	0·46	317	[31]	286	217
		O_2	17·2	0·76	383	[31]	352	205
[4]	$4 \cdot 12 \times 10^{-2}$	H_2	17·3	12·2	74	29	45	1001
		NH_3	17·4	10·05	3960	120	3840	82·3

The values given in brackets are not direct experimental values but the mean of all those obtained for small quantities of hydrogen in air, this being very nearly the same as for small quantities of air in hydrogen.

The interpretation of these results in terms of permeability, absorption coefficient, and diffusion-constant is shown in the following Table. The product P*l* is permeability reduced to a film of unit thickness. The first three columns give results in absolute units, the second three give the relative values, those for hydrogen being unity.

In the case of film (4) the values for hydrogen are the means of those obtained on the other films since the conditions of the experiment would not allow a direct test.

Gas.	Diffusion constant.	Absorption coefficient.	Permeability.
H_2	7·23 × 10^{-6} (mean)	0·0397	26·7 × 10^{-8}
CO_2	0·85 × 10^{-6}	0·86	73·4 × 10^{-8}
N_2O	0·72 × 10^{-6}	1·71	121·0 × 10^{-8}
Air	1·21 × 10^{-6}	0·043	5·18 × 10^{-8}
O_2	0·95 × 10^{-6}	0·091	8·97 × 10^{-8}
NH_3	0·074 × 10^{-6}	41·0	303·0 × 10^{-8}

Gas	Relative K.	Relative A.	Relative *Pl.*	Relative solubility in water at 15° C.	Critical temperature. ° C.
H_2	1·00	1·00	1·00	1·00	−238
CO_2	0·098	27·6	2·73	52·0	+31
N_2O	0·107	44·0	4·62	41·5	+37
Air	0·168	1·08	0·19	0·95	—
O_2	0·135	2·30	0·336	1·60	−119
NH_3	0·0117	950	11·3	40000	+131

The lag of 64 minutes for ammonia is very striking. This means that in a film of 1 mm. thickness gradients would not reach within 1 per cent. of their final values in less than eight hours. For a thickness of 1 cm. a month would be required.

It will be seen from these figures that, although some of these gases have for some time been known to pass through rubber membranes more rapidly than hydrogen, in no case is it because the material itself is more permeable to them when the melecular concentrations are the same. On the contrary, ammonia has an abnormally low diffusion constant, even after allowance is made for its greater density, as shown by the following Table:—

Gas.	Approximate relative density.	$\sqrt{d}$.	Relative K.	K$\sqrt{d}$.
H_2	2	1·4	1·00	1·4
CO_2	48	6·9	0·098	0·67
N_2O	44	6·6	0·107	0·70
Air	14·4	3·8	0·168	0·64
O_2	16	4·0	0·135	0·54
NH_3	17	4·1	0·0117	0·048

Thus, viewed in the light of Graham's Law of Diffusion, hydrogen has an abnormally high and ammonia an abnormally low diffusion-constant.

The last two columns are added to bring out the general resemblance between absorption of gases by rubber and by water, and to support the suggestion that the absorption of gases by rubber has some close connection with the nearness of the gas to its critical state. If the latter is the case we should expect that with increase of pressure the absorption, and hence the permeability, to increase more rapidly than the partial pressure of the gas. Such an effect has been observed with carbon dioxide by Prof. Dewar (21), but as the rubber film was supported on gauze with high pressure on one side it is not improbable that some of the effect at least was due to local thinning of the film due to its moulding into the irregularities of the gauze.

The similarity between the solubilities of these gases in rubber and in water may have another explanation. Prof. Dewar (22) has shown that the logarithm of the permeability of rubber to a gas varies linearly with the temperature of the rubber, but that there are different slopes of the line above and below 0° C. suggesting that absorbed water has some definite function in determining the permeability. It is also known that rubber absorbs a large quantity of water vapour and is very permeable to it. The high concentration of ammonia and other gases in rubber may possibly, then, be due to their solution by the absorbed water.

It seems clear that the process of diffusion of a gas through a rubber film is determined by two more or less separate processes. Neither of these obeys simple laws. We can hardly expect, therefore, to go very far in our understanding of the problem by studying permeability alone. Measurements must be made simultaneously on the permeability, absorption coefficient, and diffusion-constant, or, as a minimum, any two of these three quantities.

This work was carried out in the Physics Department of the University of Birmingham, and my thanks are due to Dr. G. A. Shakespear for the ready way in which he granted me every facility.

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On the Structure of the Balmer Series of Hydrogen Lines.

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Introductory.

It is well known that the spectrum of hydrogen comprises the series of lines generally known as the Balmer series, which is a prominent feature in the spectra of the stars and nebulæ, and the secondary spectrum, consisting of a vast number of lines whose presence in celestial spectra has not yet been established. The co-ordination of the secondary spectrum would appear to present great difficulties on account of its complexity, but it is perhaps remarkable that a precise knowledge of the Balmer series, which was at one time considered to be the most simple series known in spectroscopy, should still be wanting.

Balmer showed, at a time when the complexity of the lines was not yet known, that the wave-lengths could be represented with considerable accuracy by the formula $\lambda = 3646 \cdot 14 m^2/(m^2-4)$, where m takes successive integral values. Balmer's formula is a special case of the formula of Rydberg for the wave-number $\nu = \text{N}\,[1/(2+p)^2 - 1/(m+q)^2]$, where ν is the wave-number, N Rydberg's "universal" constant, and p and q are fractions appropriate to the series; this is identical with Balmer's formula when p and q are put equal to zero. Curtis* has deduced from a series of accurate measurements of the leading lines of the Balmer series that the value of Rydberg's constant N is equal to 109678·3, and that the wave-numbers of the lines cannot be represented to the degree of accuracy attained in his measurements by the simple Balmer formula. Curtis was able to represent his experimental values accurately by the formula

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* 'Roy. Soc. Proc.,' vol. 90, p. 605 (1914); vol. 96, p. 147 (1919).

$$\nu = \mathrm{N}\,[1/(2+p)^2 - 1/(m+q)^2],$$

where $p = -0{\cdot}00000383$, and q takes the value 0·0000021.

These results depend on the measurement of the "optical centre of gravity" of the lines, for it has been shown by Michelson* and in numerous later investigations that the lines are complex. Michelson deduced from the visibility curves obtained with the interferometer that the lines were close doublets, the separation of the components being 0·14 A. in the case of the line Hα, and about half that value in the case of Hβ. In the case of Hα, the intensities of the components were estimated to be in the ratio 10 : 7, the stronger component being on the less refrangible side.

The widths of the components, particularly in the case of Hβ, are of a magnitude comparable with their separation, and there is no doubt that this fact is partly responsible for the discordant values obtained by different investigators. Thus Houstoun† gives for Hα 0·065 A., Buisson and Fabry‡ 0·132, and Paschen and Back§ 0·20. The line Hα appears at best as a very diffuse and difficult doublet, and I am not aware that the doubling of Hβ has ever been seen, its structure having been deduced from the disappearance of the fringes seen with the interferometer.

In a recent investigation‖ the separations of the components of Hα and Hβ have been determined from quantitative photometric measurements of the intensity distribution given by the overlapping components, the values found being 0·132 A. for Hα, and 0·033 A. for Hβ, the former value being in exact agreement with the value given by Buisson and Fabry. These values imply that the Balmer series is to be looked on a principal series, in which the wave-number separations of the components converge to the limit of the series, rather than as a diffuse or sharp series, in which a constant wave-number difference between the components is preserved throughout the series. It must, however, be remembered that different lines in the spectrum are subject to very great variations in their relative intensities under different physical and electrical conditions of excitation, and that under certain circumstances the structure of the lines may be subject to variations. In this case a number of suggestions which have been made as to the complete representation of the series would not be excluded.

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* 'Phil. Mag.,' (5), vol. 34, p. 282 (1892).

† 'Phil. Mag.,' (6), vol. 7, p. 456 (1904).

‡ 'Journ. de Phys.,' June, 1912.

§ 'Ann. der Phys.,' vol. 39, p. 897 (1912).

‖ Merton and Nicholson, 'Phil. Trans.,' A, vol. 217, p. 237 (1917).

It has been pointed out* that if a single series of lines were represented by the formula used by Curtis,

$$\nu = \mathrm{N}[1/(2+p)^2-1/(m+q)^2],$$

another series of lines might be looked for on the basis of the combination principle which would be represented by

$$\nu = \mathrm{N}[1/(2+q)^2-1/(m+q)^2],$$

and there might also be a series

$$\nu = \mathrm{N}[1/(2+q)^2-1/(m+p)^2].$$

The lines of the first and second of these series would exhibit a constant difference in wave-number of 0·192, corresponding to wave-length separations in Hα and Hβ of 0·081 A. and 0·048 A. respectively, whilst the wave-number differences between the first and third of these series would not be constant, and would give rise to wave-length differences of 0·105 A. for Hα and 0·054 A. for Hβ. These considerations involve no new assumptions and are based on the well established combination principle, but Sommerfeld† has carried out an investigation of the origin of the Balmer series on the basis of the quantum theory, which demands an even more complex structure for the line.

Sommerfeld's theory is an extension of Bohr's theory of the hydrogen spectrum, the hydrogen atom being supposed to consist of an electron in circular or elliptical orbital motion about a positively charged nucleus, the steady states being defined by discrete values of the angular momentum and, in the case of elliptical motion, the eccentricities of the ellipses being limited to certain definite values. The precise value of the separation of the components, or principal groups of components, of the line Hα is an important constant in the numerical results deduced by Sommerfeld. Although his conclusions do not appear to be in agreement with the experimental results of a previous investigation,‡ it will be shown in a later section that the phenomena are more complex than has been supposed hitherto, and that it is probable that the structure of the lines varies under different conditions of excitation.

The Width of the Hydrogen Lines.

The sharpness of all spectrum lines is affected by the broadening due to the motion of the radiating particles in the line of sight, operating in accordance with Doppler's principle. Under certain conditions, notably when the spectrum is excited by powerful condensed electric discharges, the lines may be affected by an entirely different cause of broadening, but the motion of the atoms in the line of sight sets a very definite inferior limit to the widths of the lines. The theory of this effect has been given very completely by Lord Rayleigh,[*] who has shown that the distribution of intensity in the widened line is represented by the well known probability law $I = e^{-kx^2}$, and that the width of the line may be conveniently expressed by defining the "half-width" $\delta\lambda$ as the value of x when $I = 0{\cdot}5$, I being equal to unity at the maximum of intensity.

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* Merton and Nicholson, *loc. cit.*

† 'Sitz. der K. Bayr. Akad.,' München, 1916.

‡ Merton and Nicholson, *loc. cit.*

According to this definition Lord Rayleigh shows that

$$\delta\lambda/\lambda = (\theta/m)^{\frac{1}{2}} \times 3{\cdot}57 \times 10^{-7},$$

where θ is the absolute temperature of the gas and m the mass of the radiating particles in terms of that of the hydrogen atom. In their investigations with the interferometer Buisson and Fabry (*loc. cit.*) have shown that in the case of gases of the helium group in vacuum tubes at low pressures, and excited by uncondensed discharges, the widths of the lines are entirely, or almost entirely accounted for by the motions of the radiating particles, and that the temperature is that of the walls of the tube or not much higher. Putting $\theta = 16°$ C. the limiting half-widths of the hydrogen components for Hα are found to be $\delta\lambda = 0{\cdot}040$, and putting the separation of the components at 0·132A., and their relative intensities in the ratio 10 : 7 the intensity of the minimum between the components should be about 31 per cent. of the mean of the intensities of the two components. It is evident that the line should be seen as a fairly sharp doublet, which is certainly not the case under ordinary conditions.

On the basis taken above, the limiting half-widths of the components of Hβ should be somewhat less than 0·030A., so that it should not be difficult to see the line as a doubtlet if the distance between the components were 0·07A. or more. The appearance of Hα at once shows that these limits are not attained. Either there is in this case some cause of broadening which does not affect the lines of the rare gases or some other explanation must be sought. The former view seems unlikely, for the only cause of broadening to be suspected would be of the same type as that which occurs to a greater extent when the gas is excited to luminosity by condensed discharges, and which is now generally recognised to be due to the influence of the electric field of neighbouring charged particles on the radiating atoms, operating in accordance with the Stark effect. It is true that this effect is greater for hydrogen than for other elements, but the effect in the case of helium is comparable in magnitude and the excellent agreement between the experimentally measured widths of helium lines and the widths calculated on the basis of the Doppler effect in the experiments of Buisson and Fabry (*loc. cit.*), would seem to leave little room for broadening of this type.

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[*] 'Phil. Mag.,' vol. 29, p. 274 (1915).

The Échelon Grating.

A large number of observations of the lines Hα and Hβ were made with a Lummer Gehrcke plate, and results of some value were obtained. It was found, however, that observations could be more easily made with an échelon diffraction grating, and the structure of the lines has been investigated with an instrument of this type, having 35 plates 15·085 mm. in thickness, the step of the grating being 0·83 mm. The instrument was made by Messrs. Adam Hilger, and was mounted in the usual manner. This instrument possesses certain advantages over the Lummer Gehrcke plate in the investigation of broad lines; with the latter instrument the ratio of the resolving power to the distance between successive orders is extremely small, a fault from which the échelon suffers to a much smaller though still somewhat objectionable degree. Preliminary analysis of the light from the vacuum tubes was effected by means of a constant deviation spectroscope, the slit of the échelon spectroscope being situated at the focus of the telescope lens of the constant deviation instrument. These instruments, after the first adjustment, gave no further trouble. Measurements could be made with a micrometer eyepiece, or by substituting a camera for the eyepiece, the spectrum could be photographed.

The theory of the échelon has been given by Michelson,* but in its application to the problems under discussion certain considerations which do not usually affect the use of the instrument must be taken into account, and may, in some cases, be used to obtain information which is not usually afforded by measurements of this kind. In determining the separation of the lines of a doublet it is generally found convenient to calculate the difference in wave-length corresponding to the separation of successive orders; the distance between successive orders and between the components of the doublet being measured with a micrometer, the wave-length separation of the doublet can at once be found. The difference in wave-length ϵ corresponding to the separation of successive orders is given by the formula $\epsilon = \lambda^2/bt$, where $b = (\mu-1) - \lambda d\mu/d\lambda$; λ is the wave-length of the light, t the thickness of the plates, and μ the refractive index of the glass for wave-length λ.

Accurate measurements of the refractive index of the glass for the lines

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* 'Astrophys. Journ.,' vol. 8, p. 36 (1898).

C, D, F, and G were furnished by the makers, and it was found that the relation of refractive index to the wave-length could be accurately represented by the formula, due to Hartmann, $\mu = \mu_0 + C/(\lambda - \lambda_0)$, where μ_0 C and λ_0 are constants, $d\mu/d\lambda$ being thus equal to $-C/(\lambda-\lambda_0)^2$. The above method of determining the difference in wave-length of the components of a doublet is, however, only strictly applicable in the case of lines of insignificant width, a condition by no means satisfied by the hydrogen components. This arises in the following manner: The distribution of intensity by the échelon is given by the formula

$$I_n = [\sin^2 \pi (s/\lambda)\,\theta]/[\pi (s/\lambda)\,\theta]^2$$

where s denotes the step of the grating and θ the angle of diffraction. Thus $I = 1$ when $\theta = 0$, and $I = 0$ when $\theta = \lambda/s$. If the maximum of a particular order falls at $\theta = 0$ the two neighbouring orders are absent since the angular separation of successive orders is equal to λ/s. Putting $\pi (s/\lambda)\,\theta = \alpha$ the formula for the intensity distribution becomes $I_n = \sin^2\alpha/\alpha^2$.

By a slight rotation of the échelon a line may be set in the single order position, when $\alpha = 0$, and only one order is visible, or in the double order position when two orders of equal intensity (with faint orders on either side) can be seen at $\alpha = \pm\pi/2$, or in any desired intermediate position. It is now evident that a line which is not in the single order position ($\alpha = 0$) will suffer an apparent displacement, in so far as the maximum of intensity is concerned, towards the point $\alpha = 0$ by an amount depending on the width of the line. Assuming that the width of the line is due to the Doppler effect, the intensity distribution in the line is given by $I = e^{-kx^2}$, where x may, for convenience, be expressed in circular measure.

The apparent maximum of a line does not occur at the point defined by $x = 0$, but at the point at which $dI/dx = dI_n/d\alpha$, or $(\alpha \sin 2\alpha - 2\sin^2\alpha)/\alpha^3 = 2kxe^{-kx^2}$. This gives the solution for the displacement; but for practical purposes the following application is important. It has been found that the *échelon* can be set in the double order position with considerable precision. It can be easily shown that a small error in the setting is unimportant. Let the distance between the maxima of the two orders in the double order position be P. Then the displacement ξ of each order in the direction of $\alpha = 0$ is given by $\xi = (\pi - P)/2$. Then $(m \sin 2m - 2\sin^2 m)/m^3 = 2k\xi e^{-k\xi^2}$, where $m = (\pi/2) - \xi$.

It has been found that this equation can readily be solved, with an accuracy transcending the requirements of practical measurement, by the following simple interpolation formula: Let δx be the half-width of the line in radians, *i.e.*, the value of x when $e^{-kx^2} = 0{\cdot}5$. Then $\delta x = 1{\cdot}6\,\xi^{\frac{1}{2}}$. Since $\xi = (\pi - P)/2$ and P is measured on the micrometer, it remains only to calibrate the micrometer in radians. This can be readily accomplished by measurements of the separation of successive orders of such lines as the satellites of the green mercury line, $\lambda = 5461$ A., whose width is so small that the value of ξ is insignificant. Since the micrometer measures linear distances at the focus of the telescope objective, a small correction may be necessary if the difference in focal length of the telescope lens for the green line of mercury and the line under consideration is appreciable. This may be determined with precision by measurements of the lengths of the lines with the micrometer, the length of the lines being limited by the wedge used for varying the effective length of the *échelon* slit. Let L_g be the length of the mercury line, $\lambda = 5461$ A., on the plate in terms of the micrometer readings, and L_λ the length of a line of wave-length λ, and let Q_g be the difference between the micrometer readings of successive orders of a mercury satellite and Q_λ, the corresponding distance for wave-length λ. Then $Q_\lambda = (Q_g \times \lambda \times L_\lambda)/(5461 \times L_g)$.

It thus appears that the corrections to be applied in the case of broad lines may be turned to advantage, since they give an estimate of the physical widths of the lines. It is also possible to measure the relative intensities of the components of a doublet with some precision. The procedure in the case of a doublet λ_1 and λ_2 is as follows: The value of δx, and thence the value of k, is determined from measurements of the separation of the orders in the double order position for λ_1. The separation of the components $\lambda_1 - \lambda_2$ is then measured, and from the value of k the displacements of the maxima from the true centres of the lines can be calculated. In many cases the differences between the displacements is insignificant, and the separation of the components in wave-lengths can at once be found when the true separation of successive orders in terms of the micrometer divisions has been determined from measurements of the separation of the orders for a line of negligible width.

For the measurement of the relative intensities, the *échelon* is set to the single order position for λ_1, and the crosswires of the micrometer eye-piece are set on to the maximum of the line λ_1. The *échelon* is then rotated until the maxima of λ_1 and λ_2 appear to be of the same intensity. Let their positions, reduced to radians, be α_1 and α_2. The relative intensities I_1 and I_2 are then given by $I_1/I_2 = [\sin^2 \alpha_2/\alpha_2{}^2]/[\sin^2 \alpha_1/\alpha_1{}^2]$. Strictly speaking, the displacements ξ_1 and ξ_2 should be taken into account, the true centres of the lines being situated at $\alpha_1 + \xi_1$ and $\alpha_2 + \xi_2$, the relative intensities being given by the formula

$$I_1/I_2 = [e^{-k\xi_2^2} (\sin^2 \alpha_2/\alpha_2^2)]/[e^{-k\xi_1^2} (\sin^2 \alpha_1/\alpha_1^2)],$$

but the accuracy attained in photometric measurements does not generally call for the use of the more rigorous expression.

Experimental Observations.

In the investigation previously referred to,* which related to the structure of the lines Hα and Hβ, the vacuum tubes which were used were filled with hydrogen at a low pressure, without any very special precautions. I have since noticed on numerous occasions that the behaviour of the line Hα, as seen under a high dispersion, has been very capricious. Sometimes the doubling was fairly distinct, whilst at other times, under conditions of electrical excitation which did not appear to be dissimilar, it seemed as if all definite structure had vanished, and only a broad unsymmetrical line could be seen. Attempts to control these changes by varying the pressure in the discharge tube and by altering the conditions of excitation were nugatory, but there remained the possibility that the changes which occurred might be referred to the influence of other gases which were present in the discharge tube. It has been shown in previous investigations† that the presence of impurities, notably helium, may give rise to alterations in the distribution of intensity in the spectrum, and that, under certain conditions, the secondary spectrum of hydrogen may be modified to a profound extent.

Further investigation in this direction at once showed that the structure of the Balmer lines is affected by the presence of impurities, and, since it has been found possible to observe the lines Hα and Hβ as distinct doublets, which, by a change in the conditions, are transformed into broad unsymmetrical lines, in which no definite structure can be detected, I have attempted in the first place to describe qualitatively the character of these changes, and in the second to isolate the conditions for obtaining the sharpest resolution of the lines, and to measure with the greatest possible accuracy the separation of these components under these conditions.

Qualitative.

Observations have been made at the temperature of the laboratory, and also with the capillaries of the vacuum tubes cooled to the temperature of liquid air. With tubes of the H form, the latter condition was attained by making a trough of indiarubber round the capillary of the tube, and keeping this trough filled with liquid air during the experiment. That this procedure was effective will be seen from the results of quantitative measurement. Vacuum tubes containing very pure hydrogen were prepared by heating in a flame of hydrogen a palladium tube, which was connected with the previously exhausted tubes; by repeatedly admitting hydrogen in this way, and removing it again by pumping, the impurities could be washed out, and it is believed that the tubes filled in this way were very free from contamination.

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* Merton and Nicholson, *loc. cit.*

† Merton and Nicholson, 'Phil. Trans.,' A, vol. 220, p. 137 (1919); 'Roy. Soc. Proc.,' A, vol. 96, p. 112 (1919); Merton, 'Roy. Soc. Proc.,' A, vol. 96, p. 382 (1920).

It is known that, in very pure hydrogen, the intensity of the lines of the Balmer series is greatly reduced relatively to those of the secondary spectrum, and, in the tubes prepared in the manner described, the effect is very striking. With these tubes the line Hα appears as a fairly broad unsymmetrical line, showing no evidence of doubling, and the appearance of Hβ is very similar. At the temperature of liquid air, there is, perhaps, just an indication of structure in Hα. It has already been pointed out that the "half-width" of the components of Hα at room temperature should be 0·040 A. if the broadening is entirely due to the motions of the radiating particles. At the temperature of liquid air, the "half-width" should be reduced to 0·023 A. The corresponding values for Hβ are 0·030A. and 0·017 A. respectively. With a small trace of impurity, such as water vapour, or in tubes showing the Ångström carbon bands, traces of structure in Hα are apparent at ordinary temperatures, though Hβ still shows no sign of resolution. In tubes filled with water vapour, Hα appears as a fairly distinct doublet. Cooling with liquid air, as, indeed, might be expected, is ineffective in improving the definition, the necessary impurities being, in fact, frozen out by this procedure.

It is important to note that the total width of the doublet seemed to be greater than the width of the unresolved line seen in pure hydrogen. In tubes containing a mixture of hydrogen and helium at a few millimetres pressure the resolution of Hα is complete, while Hβ still shows no definite structure. With these tubes, however, the advantages of cooling to the temperature of liquid air are fully realised, for the helium, unlike carbon compounds and water vapour, is not removed from the mixture, and under these conditions Hα appears as a sharp doublet, perfectly resolved, and almost reminiscent of the appearance of the D lines in a diluted sodium flame when seen under a lower dispersion. Hβ appears as a perfectly definite doublet but the components are not completely resolved and are hazy in appearance. The proportions of helium and hydrogen necessary for exhibiting these phenomena are not closely restricted, and no definite changes can be observed over a wide range of pressure so long as the helium is present in excess. It is perhaps remarkable that the doubling of Hα at ordinary temperatures is quite clean with tubes filled at pressures as great as 40 mm. of mercury, the proportion of helium to hydrogen in these tubes being estimated to be in the ratio 80 : 1.

The qualitative observations appear to be in accord with the results of the previous investigation,* but they show that these results refer to vacuum tubes containing hydrogen with a small trace of impurity; with the tubes containing a mixture of hydrogen and helium it is at once evident that the structure of both Hα and Hβ, and not merely the width of the components, has undergone a striking change. The appearance of Hα is in fact the most sensitive criterion for the purity of the hydrogen, though the colour of the discharge becomes almost white at a stage in the purification at which spectrum lines due to impurities appear to be entirely absent. A small trace of impurity can be removed by passing a heavy current through the tube so that a deposit of aluminium from the electrodes is formed on the walls of the tube. This layer of sputtered aluminium, as is well known, removes traces of carbon compounds and other impurities, and it is thus possible to watch the change in the line Hα during the process of purification.

Quantitative.

It has already been stated that the conditions of sharpest resolution are attained by cooling a mixture of helium and hydrogen at a few millimetres pressure to the temperature of liquid air, and it has been under these conditions that the quantitative measurements here recorded have been made. An enlarged reproduction of photographs showing Hα and Hβ is given in fig. 1. The enlargement, showing one order only, was made with

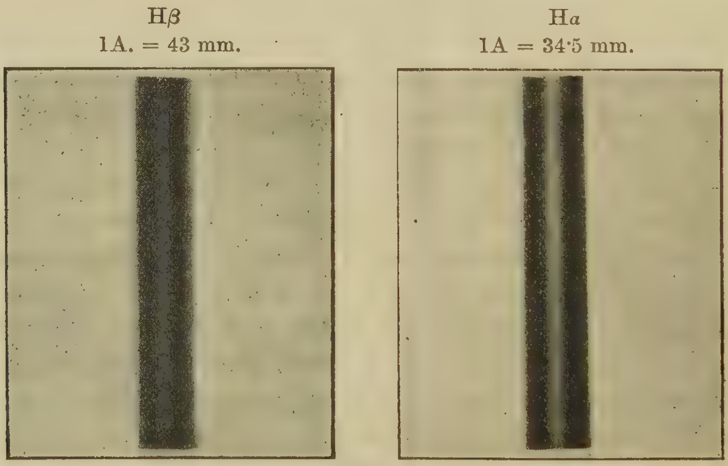

Fig. 1.

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* Merton and Nicholson, *loc. cit.*

the aid of a cylindrical lens in the optical train to eliminate the grain of the plate. Measurements were made with a Hilger photo-measuring micrometer of three plates of Hα and four of Hβ, and the results given for each plate were taken from the mean of six sets of micrometer readings. A plate was also taken of the mercury green line ($\lambda = 5461$A.) for purposes of calibration. The method of reducing the measurements has been given in a previous section, and the numerical results, using the same notation, are as follows:—

Mercury $\lambda = 5461$A.

Separation of orders in micrometer divisions = 751
Length of lines in micrometer divisions = 4503

Hα

Separation of components.	Separation of orders.	Length of lines.
275	890	4485
276	890	4470
271	889	4478
Mean = 274	890	4478

If the components were of vanishingly small width the separation of the orders should be

$$Q_{H\alpha} = (751 \times 6563 \times 4478)/(5461 \times 4503) = 898,$$

$$\xi_1 = 8\pi/(898 \times 2) = 0{\cdot}0140 \text{ radian}, \quad \delta\alpha = 1{\cdot}6\sqrt{0{\cdot}014} = 0{\cdot}1894 \text{ radian}.$$

$$\epsilon_{H\alpha} = 0{\cdot}4721\text{A}, \quad \delta\lambda = (0{\cdot}1894 \times 0{\cdot}4721)/\pi = \mathbf{0{\cdot}028A}.$$

Apparent maximum of 1st component is at $(\pi/2) - 0{\cdot}0140 = 1{\cdot}5568$,

Apparent maximum of 2nd component is at $1{\cdot}5568 - (274\pi/898) = 0{\cdot}5982$,

$$dI_n/d\alpha_{(\alpha = 0{\cdot}5982)} = 0{\cdot}36.$$

From the value $\delta\alpha = 0{\cdot}1894$ the value of the constant k in the intensity distribution formula $I = e^{-k\alpha^2}$ is found to be $k = 19{\cdot}32$ and from the relation

$$2k\xi_2 e^{-k\xi_2^2} = dI_n/d\alpha, \quad \xi_2 = 0{\cdot}0093.$$

True maximum of 1st component is at $\pi/2 = 1{\cdot}5708$,

True maximum of 2nd component is at $0{\cdot}5682 + 0{\cdot}0093 = 0{\cdot}6075$,

Difference = 0·9623 radian.

Since $\epsilon_{H\alpha} = 0{\cdot}4721$, the separation of the components is equal to

$$(0{\cdot}9623 \times 0{\cdot}4721)/\pi = \mathbf{0{\cdot}1446A}.$$

It so happened that, in the double order position, the intensities of the two components appeared to be identical, and the relative intensities could be calculated without further measurement. To a relevant degree of accuracy, the relation of the intensities is thus given by

$$I_{\lambda_1}/I_{\lambda_2} = [\sin^2 0{\cdot}6075/0{\cdot}6075^2]/[\sin^2 1{\cdot}5708/1{\cdot}5708^2] = 2{\cdot}18.$$

The intensities are thus in the ratio **10 : 4·6**.

Hβ

Separation of components.	Separation of orders.	Length of lines.
253	632	4559
225	603	4557
231	613	4556
256	625	4569
Mean = 241	618	4560

$$Q_{H\beta} = (751 \times 4860 \times 4560)/(5461 \times 4503) = 677.$$

$$\xi_1 = 59\pi/(677 \times 2) = 0{\cdot}1369 \text{ radian}, \quad \delta\alpha = 1{\cdot}6\sqrt{0{\cdot}1369} = 0{\cdot}592 \text{ radian}.$$

$$\epsilon_{H\beta} = 0{\cdot}2413\text{A}, \qquad \delta\lambda = (0{\cdot}592 \times 0{\cdot}2413)/\pi = \mathbf{0{\cdot}045A}.$$

Apparent maximum of 1st component is at $1{\cdot}5708 - 0{\cdot}1369 = 1{\cdot}4339$,

Apparent maximum of 2nd component is at $1{\cdot}4339 - (241\,\pi/677) = 0{\cdot}3156$,

$$dI_n/d\alpha_{(\alpha = 0{\cdot}3156)} = 0{\cdot}204, \qquad \xi_2 = 0{\cdot}0504.$$

True maximum of 1st component is at $\pi/2 = 1{\cdot}5708$,

True maximum of 2nd component is at $0{\cdot}3156 - 0{\cdot}0504 = 0{\cdot}3660$,

Difference = 1·205 radian.

Since $\epsilon_{H\beta} = 0{\cdot}2413$A, the separation of the components is equal to

$$(1{\cdot}205 \times 0{\cdot}2413)/\pi = \mathbf{0{\cdot}093A}.$$

Whilst the sharpness of the components of Hα made accurate micrometer settings an easy matter, those of Hβ were very difficult to measure; this is shown by the inferior agreement in the case of Hβ of the results for different plates, and a measurement of the relative intensities of the components has not been attempted.

Discussion.

The results obtained in the preceding section may be summarised as follows:—

Hα. Separation of components .... = 0·145A.
Half-width of components .... = 0·028A.

Intensities of the components are in the ratio 10 : 4·6.

Hβ. Separation of components .... = 0·093A.
Half-width of components .... = 0·045A.

In the case of Hα the two components are very sharply defined, and any additional components must be either of vanishingly small intensity or at an exceedingly small distance from the main components under the conditions of the experiment, for the value found for the half-width, $\delta\lambda$ = 0·028A., is very close to the theoretical value 0·023A. On the other hand, the half-width of the components of Hβ, $\delta\lambda$ = 0·045A., though of doubtful accuracy, is much in excess of the theoretical value $\delta\lambda$ = 0·017A., a result which might well be accounted for by the disturbing influence of one or more weak additional components. If the series, under the conditions of experiment, consisted of doublets of constant wave-number difference, a difference in wave-length of 0·145 A. between the components of Hα would lead to a corresponding difference between the components of Hβ of about 0·08 A.

The experimental value for Hβ, 0·093 A., would not appear to negative this arrangement, when it is borne in mind that accurate measurements of the components of Hβ are difficult, and, as St. John and Ware* have shown, micrometer measurements of incompletely resolved lines lead to values of the separation which are too high. The observed separation and the half-width found for Hβ show that the components are, in fact, nearer to the limit of resolution than the photographs would lead one to expect, the contrast being somewhat enhanced by the photographic plate. Although it is impossible to attach great weight to the exact numerical values obtained for Hβ, it is evident that the separation is of a magnitude appropriate to a diffuse or sharp series. It is believed that considerable weight may be attached to the value given for the separation of the components of Hα, for they were completely resolved and well defined, and were therefore not exposed to sources of error, which may perhaps have affected the accuracy of measurement in the case of Hβ.

These results, which were obtained with tubes containing a mixture of hydrogen and helium, are not in accordance with observations made with tubes containing pure hydrogen, or hydrogen with a small amount of impurity. The separation of the components of Hα appears to become smaller as the gas is purified, and the minimum between the components becomes brighter, to an extent which seems quite out of proportion. The appearance of both Hα and Hβ in hydrogen of the highest degree of purity does not suggest unresolved doublets with broad components of the separations given above, but is rather in accordance with doublets of a somewhat smaller separation in the case of Hα, and a considerably smaller separation in the case of Hβ, the components being in neither case resolved.

Taking all these results into consideration it seems that the structure of the lines must be complex, for it does not appear possible to explain the observations on the basis of simple doublets. If, however, it may be assumed that the lines consist of three or more components which vary in their relative intensities under different conditions, the changes which have been observed can be easily explained, and would, I think, be in harmony with Sommerfeld's (*loc. cit.*) theoretical deductions if the changes in the relative intensities of the components under different conditions is not incompatible with his theory. There is a considerable amount of experimental evidence which affords some justification by analogy for this assumption, for there are several instances in which this very phenomenon has been observed. King* has found that the red lithium line, $\lambda = 6708$ A., may appear as a doublet or as a triplet under different conditions both in the arc and also in the tube furnace, in which a change in the structure of the line due to an electrical resolution would appear to be excluded. Fabry† has shown that under different conditions in vacuum tubes the cadmium line, $\lambda = 5086$ A., may appear either as a doublet or as a triplet, and Gale and Lemon‡ have observed similar phenomena in the satellites of the green mercury line $\lambda = 5461$ A.

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* 'Astrophys. Journ.,' vol. 44, p. 15 (1916).

There is thus a considerable amount of evidence that the fine structure of lines is not invariable, and though it cannot be claimed that the exact nature of the variation in the structure of the lines $H\alpha$ and $H\beta$ has been established it seems probable that each of these lines consists of three (or perhaps more) components which show very great variations in their relative intensities under different conditions; one of these components in $H\alpha$ and one in $H\beta$ appear to be separated from the main components of the lines by a constant difference in wave-number, these components being prominent in impure hydrogen, and especially in a mixture of hydrogen and helium, whilst the other components, which are enhanced in very pure hydrogen, are separated from the main components by differences in wave-number which are more appropriate to a principal series. This explanation would not, I believe, be inconsistent with Sommerfeld's theory, and would be in complete harmony with the experimental results.

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* 'Astrophys. Journ.,' vol. 44, p. 169 (1916).

† 'Astrophys. Journ.,' vol. 9, p. 116 (1904).

‡ 'Astrophys. Journ.,' vol. 31, p. 78 (1910).

Diamagnetism due to Free Electrons.

By H. A. Wilson, F.R.S., Rice Institute, Houston, Texas, U.S.A.

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According to the electron theory of the electrical and thermal properties of metals, these bodies contain a large number of negative electrons, which move about between the metallic atoms like the molecules of a gas.

This theory explains satisfactorily several of the fundamental facts, such as the emission of electrons from hot metals, Ohm's law, and Wiedemann and Franz's law, but fails in its simple form to account for the different values of the Hall effect and other phenomena. More elaborate forms of the electron theory, based on the quantum hypothesis, enable some of these difficulties to be removed.

It seems probable that metals do contain free electrons, but the theory of the motion of these electrons, in the crystals of which solid metals are composed, has not yet been worked out in a sufficiently complete manner to account quantitatively for all the phenomena. Kent* shows that the electron theory agrees well with the facts in the case of the optical properties of some liquid metals at 400° C.

In this paper it is shown that the presence of the free electrons in a metal should produce diamagnetic susceptibility of amount comparable with that found in the diamagnetic metals.

The total magnetic susceptibility of metals is therefore presumably equal to the sum of that due to the atoms, which may be either paramagnetic or diamagnetic, and that due to the free electrons.

Let u, v, and w be the velocity components of an electron parallel to axes x, y, and z. Let there be a magnetic field of strength, H, parallel to the z axis. The equations of motion of an electron are then

$$m\dot{u} = \mathrm{H}ev,$$

$$m\dot{v} = -\mathrm{H}eu,$$

$$m\dot{w} = 0,$$

where e is the charge on an electron and m its mass. These equations give, putting $\mathrm{H}e/m = \omega$,

$$u = \mathrm{A}\sin(\omega t+\alpha),$$

$$v = \mathrm{A}\cos(\omega t+\alpha),$$

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* 'Physical Review,' December, 1919.

where α is a constant and $A^2 = u^2+v^2$, so that A is the velocity in the xy plane.

If p denotes the angular momentum of the electron about the z axis, we have

$$p = m(vx-uy) = m(xA\cos(\omega t+\alpha)-yA\sin(\omega t+\alpha)).$$

Let x_1, y_1 be the co-ordinates of the electron at the time $t = 0$, so that

$$x = x_1+\frac{A}{\omega}\cos\alpha-\frac{A}{\omega}\cos(\omega t+\alpha),$$

$$y = y_1-\frac{A}{\omega}\sin\alpha+\frac{A}{\omega}\sin(\omega t+\alpha).$$

Substituting these values of x and y in the expression for p, we obtain

$$p = m\left\{Ax_1\cos(\omega t+\alpha)-y_1A\sin(\omega t+\alpha)+\frac{A^2}{\omega}(\cos\omega t-1)\right\}.$$

Suppose that there are a very large number, n, of electrons, describing free paths like the molecules of a gas, but all moving with the same resultant velocity, V, and consider the total angular momentum of all the electrons about the z axis.

For each electron, let t be the time since its last collision with an atom, so that x_1, y_1 give its position at its last collision. Then it is easy to see that in Σp the terms $\Sigma mAx_1\cos(\omega t+\alpha)$ and $\Sigma mAy_1\sin(\omega t+\alpha)$ will be equal to zero, so that

$$\Sigma p = m\Sigma\frac{A^2}{\omega}(\cos\omega t-1).$$

The mean value of $mA^2(\cos\omega t-1)/\omega$ during a free path of duration τ is

$$\frac{mA^2}{\omega\tau}\int_0^\tau(\cos\omega t-1)\,d\tau = \frac{mA^2}{\omega}\left\{\frac{\sin\omega\tau}{\omega\tau}-1\right\}.$$

The number of free paths with times between τ and $\tau+d\tau$ out of a total number, N, is $N\epsilon^{-\tau/T}d\tau/T$, where T denotes the mean value of τ.

The average value of $\frac{mA^2}{\omega}\left\{\frac{\sin\omega\tau}{\omega\tau}-1\right\}$ for one electron during a long time is therefore

$$\int_0^\infty\frac{1}{T^2}\epsilon^{-\tau/T}\tau\frac{mA^2}{\omega}\left(\frac{\sin\omega\tau}{\omega\tau}-1\right)d\tau = -\frac{mA^2\omega T^2}{1+\omega^2T^2}.$$

Hence
$$\Sigma p = -\frac{m\omega T^2}{1+\omega^2T^2}\Sigma A^2.$$

But, since the electrons are as likely to be moving in one direction as another, the average value of A^2 must be $\frac{2}{3}V^2$, so that

$$\Sigma p = -\frac{2}{3}\frac{nm\omega V^2T^2}{1+\omega^2T^2}.$$

If λ denotes the length of the mean free path, then, since all the electrons are supposed to be moving with the same velocity, V, we have $\mathrm{VT} = \lambda$, so that

$$\Sigma p = -\tfrac{2}{3}\frac{nm\omega\lambda^2}{1+\omega^2\lambda^2/\mathrm{V}^2}.$$

Now, $\omega\mathrm{T}$ will nearly always be small compared with unity, and λ in a metal is probably nearly independent of V, so that, if the electrons, instead of all having the same velocity, have velocities distributed according to Maxwell's law, it will be very nearly correct to put

$$\Sigma p = -\tfrac{2}{3}\frac{nm\omega\lambda^2}{1+\omega^2\lambda^2/\mathrm{V}^2},$$

where V^2 now denotes the mean value of the square of the velocity. If we take n to be the number of free electrons in unit volume of the metal, then Σp will be the angular momentum, about any axis parallel to the magnetic field, of the free electrons per unit volume.

The motion of the electrons with this angular momentum produces a magnetic field opposite in direction to the external field H.

Consider a bar of the metal, of circular cross-section, with its axis parallel to the magnetic field H. The angular momentum and magnetic field due to the motion of the electrons in this bar will be equal to those due to a current circulating round the surface of the bar in planes perpendicular to its axis. Let this current be i per unit length along the axis, and let the number of electrons carrying this current be N per unit area. The angular momentum of these electrons about the axis of the bar is $2\pi r^2\mathrm{N}mv$, where v is their velocity. The angular momentum per unit volume is therefore $2\pi r^2\mathrm{N}mv/\pi r^2 = 2\mathrm{N}mv$. Also, $i = \mathrm{N}ev$, so that $2\mathrm{N}mv = 2mi/e$.

The magnetic field inside the bar due to the current i is equal to $4\pi i$, so that the magnetic moment per unit volume is $4\pi i \,.\, \pi r^2/4\pi \,.\, \pi r^2 = i$. Hence the intensity of magnetisation $\mathrm{I} = i$. The angular momentum per unit volume is therefore equal to $2m\mathrm{I}/e$. It can easily be shown that this result is true for a bar of any cross section.

Hence $$\mathrm{I} = \frac{e}{2m}\Sigma p = -\tfrac{1}{3}\frac{ne\omega\lambda^2}{1+\omega^2\mathrm{T}^2}.$$

Since $\omega = \mathrm{H}e/m$ this gives for the susceptibility

$$s = \frac{\mathrm{I}}{\mathrm{H}} = -\tfrac{1}{3}\frac{ne^2\lambda^2}{m(1+\omega^2\mathrm{T}^2)}.$$

In the case of most diamagnetic metals $\omega\mathrm{T}$ is probably very small compared with unity, so that approximately

$$s = -\tfrac{1}{3}\frac{ne^2\lambda^2}{m}.$$

In this case we should not expect s to vary much with the temperature, since λ probably does not vary much. At very low temperatures, with large values of H, $\omega \mathrm{T} = \omega\lambda/\mathrm{V}$ cannot be neglected, and the expression for s indicates that s should diminish and become zero at the absolute zero of temperature.

According to the electron theory we have $\sigma_{\mathrm{H}} = ne^2\mathrm{T}/(m(1+\omega^2\mathrm{T}^2))$, where σ_{H} denotes the conductivity in a transverse magnetic field H and $\omega = \mathrm{H}e/m$ as before. In this expression for σ_{H} as in that for s the value of T is probably not the same as when there is no magnetic field. We have

$$\frac{s}{\sigma_{\mathrm{H}}} = -\frac{\mathrm{V}\lambda}{3} = -\frac{\mathrm{V}^2\mathrm{T}}{3}.$$

If p denotes the pressure of a gas of density ρ, the molecules of which have the same mass as negative electrons, then $p = \frac{1}{3}\rho\mathrm{V}^2$, so that

$$\frac{s}{\sigma_{\mathrm{H}}} = -\frac{p\mathrm{T}}{\rho}.$$

This equation suggests that s should be nearly proportional to σ_{H}. In the case of most metals, σ_{H} differs so little from σ_0 that the corresponding variations in s are quite inappreciable; but in the case of bismuth σ_{H} in strong fields is much less than σ_0, so we might expect the susceptibility of bismuth to be less in strong fields. Faraday thought he observed such a diminution, but Wills* found s constant up to $\mathrm{H} = 10{,}000$. Wills' experiments seems to be the only ones in which strong enough fields were used to give an appreciable diminution in the conductivity.

At 0° C. if $p = 1{\cdot}013 \times 10^6$ dynes per sq. cm. we have

$$\rho = 0{\cdot}00009 \times \tfrac{1}{2} \times \frac{1}{1870} = 2{\cdot}4 \times 10^{-8} \text{ gram. per c.c.}$$

Hence

$$\frac{s}{\sigma_{\mathrm{H}}} = -4{\cdot}23 \times 10^{13}\mathrm{T}.$$

The following Table gives some values of s and σ_{H}, and the corresponding values of T. The values of T deduced from the optical properties are given under T′, and those deduced from the effect of a magnetic field on the conductivity under T″:—

Substance.	$-s \times 10^6$.	$\sigma \times 10^6$.	T.	T′.	T″.
Bismuth	15	9	4×10^{-14}	10^{-15}	3×10^{-12}
Bismuth (liquid at 400° C.)...	0·4	8	8×10^{-16}	10^{-16}	—
Mercury	2·5	10·6	6×10^{-15}	2×10^{-16}	$2 + 10^{-14}$
Silver	1·5	670	5×10^{-17}	2×10^{-14}	$2 + 10^{-14}$

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* 'Phil. Mag.,' vol. 45, p. 432 (1898).

The values of s and σ are those given in Landolt and Börnstein's Tables. T′ for bismuth is approximately the value given by Drude's optical measurements, from which the values of T′ for mercury and silver are also deduced. The value of T′ for liquid bismuth is that given by C. V. Kent.* The value of T″ for bismuth is got from observations by C. W. Heaps,† and that for silver from those of Patterson.‡

In the cases of solid bismuth and mercury, the value of T, calculated from the susceptibility, is between the other two values, which differ widely. In the case of liquid bismuth, T is eight times T′. For silver, T, from the susceptibility, is much smaller than the other two estimates.

The conductivity is proportional to nT, so that, for a given conductivity, s, as calculated, varies directly as T or inversely as n. It follows that, to account for the small susceptibility of metals like silver, the number of free electrons would have to be supposed much greater than the estimates derived from optical and magnetic data. This may be due to the atoms being paramagnetic, so that most of the diamagnetism due to the free electrons is neutralised.

It appears that metals containing few free electrons should be more diamagnetic than those containing many. Thus bismuth and antimony, which seem to contain comparatively few free electrons, are strongly diamagnetic. The same is true of mercury. Also, fused bismuth apparently contains many more free electrons than solid bismuth, and is much less diamagnetic.

If $\sigma_H = \sigma_0 + \delta\sigma$ we have, if T is supposed to be independent of H

$$\frac{\delta\sigma}{H^2\sigma_0} = \frac{-e^2T^2}{m^2(1+\omega^2T^2)}.$$

Putting $\delta\sigma/H^2\sigma_0 = A$ we get

$$\frac{s}{A} = \frac{nmV^2}{3},$$

so that s/A is equal to the gas pressure in the metal due to the free electrons.

The values given for s, σ and A lead to the equation

$$\frac{-s}{\sigma\sqrt{(-A)}} = \frac{1}{3}\frac{mV^2}{e} = \frac{p_0}{n_0 e},$$

where p_0 is the pressure in a gas containing n_0 molecules per cubic centimetre.

According to this, $-s/\sigma\sqrt{(-A)}$ should be a constant, having the same value for all substances. In electromagnetic units, p_0/n_0e is equal to $2{\cdot}5 \times 10^6$

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* 'Physical Review,' December, 1919.

† 'Physical Review,' October, 1917.

‡ 'Phil. Mag.,' vol. 3, p. 643 (1902).

approximately at 0° C. The values of $-s/\sigma\sqrt{(-A)}$ for different diamagnetic substances, calculated from the experimental values, are much smaller than $2{\cdot}5 \times 10^6$. This indicates possibly that the kinetic energy of the electrons in a metal is much less than that of the molecules of a gas at the same temperature. Another way of explaining the difference is to suppose that the atoms are paramagnetic, so that s is smaller than that due to the free electrons alone.

In conclusion, it may be said that, while the theory indicates clearly that free electrons should produce diamagnetic susceptibility, the electron theory of the optical and electrical properties of metals is not in a sufficiently satisfactory condition to provide reliable data with which to compare results deduced from the observed susceptibilities.

The Pressure upon the Poles of Metallic and Composite Arcs, including an Enquiry into the Reactions consequent upon Electron Emission.

By W. G. Duffield, D.Sc., Professor of Physics, T. H. Burnham, B.Sc., and A. H. Davis, B.Sc., Post-Graduate Students in Physics, University College, Reading.

(Communicated by Prof. O. W. Richardson, F.R.S. Received December 16, 1919.)

Experiments upon the pressure experienced by the poles of a carbon arc* led to the theory, which was put forward tentatively, that it was due to the recoil consequent upon the projection of electrons from the poles. Experiments have subsequently been made upon metallic arcs, using poles of iron, silver, copper, and an alloy of silver and copper, and also upon a composite arc in which one pole was of silver and the other of carbon.

In dealing with the carbon arc it was found possible to eliminate the effects of the electromagnetic influence of the rest of the circuit and of the earth's magnetic field, by employing what was called the double-arc method; but in the present set of experiments the rapid melting of the metal rods made it expedient in the majority of cases to employ the less direct single-arc method, which had also been used in the carbon investigation, the necessary allowances for the disturbing influences being made in the manner already described. In the case of the copper arc a satisfactory series was also obtained by using the two arcs.

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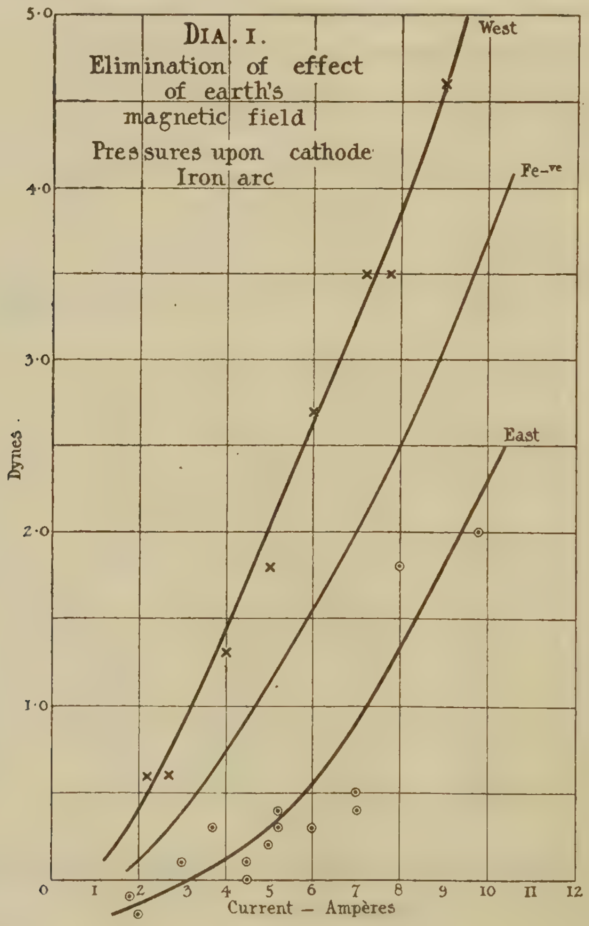
* Duffield, Burnham and Davis, 'Phil. Trans.,' vol. 220, p. 109 (1919).

The first set of observations was obtained by Mr. Thos. H. Burnham, B.Sc., and the second set by Mr. A. H. Davis, B.Sc. The technique involved in the measurement of such a small force as the fraction of a dyne was difficult to acquire, but the earlier experiments upon carbon arcs which were carried out by the writer and these two observers provided the necessary and indispensable experience. In order to show how the results were arrived at typical series of observations are recorded in Table I (Burnham, single-arc method) and Table II (Davis, double-arc method). In the former method the suspension, which was bifilar, suffered to a small extent from the fact that the constant altered slightly as the material of the suspended pole burnt away and lightened the load. At the top of the first Table is set forth the weight of the suspended portion of the apparatus, the distance apart of the fibres at the top (a) and at the bottom (b), the length of the arm measured from the centre of the suspension to the centre of the metallic pole, and the length of the two fibres. In order to vary the sensitivity, a and b were suitably altered.

Table I.—Single Arc Method. Observer, Mr. Burnham. Silver Arc. Pressure upon Anode.

Current in amps.	P.D. in volts.	Arc length in mm.	θ Twist.	Total pressure in dynes.	Pressure corrected for earth's field.	Pressure corrected for earth's field and electromagnetic effect.
A.—Cathode on East.						
Weight 25·95 grm., a = 0·8 cm., b = 0·5 cm., arm = 9·7 cm., length of fibres 38·5 cm.						
2·0	42	3·5	2·5	0·3	0·1	0·06
2·8	34	3·5	4·0	0·5	0·2	0·12
3·8	32	3·5	8·0	1·0	0·5	0·29
5·0	26	3·5	13·0	1·6	0·9	0·64
6·2	25	3·5	22·0	2·6	1·5	1·08
6·4	30	3·5	23·0	2·7	1·6	1·15
8·6	20	3·5	45·5	4·9	3·0	2·14
9·4	25	3·5	50·5	5·3	3·6	2·59
B.—Cathode on West.						
Weight 28·35 grm., a = 0·8 cm., b = 0·5 cm., arm = 9·7 cm., length of fibres 38·35 cm.						
2·0	50	3·4	−1	−0·1	0·1	0·06
2·0	50	3·4	−2	−0·3	0·1	0·06
3·0	46	3·4	0	0·0	0·3	0·15
3·0	32	3·4	−4	−0·5	0·3	0·15
4·0	32	3·4	0	0·0	0·6	0·39
5·0	32	3·4	1	0·1	0·9	0·64
9·0	24	3·4	15	2·0	3·3	2·36

The column headed "twist" indicates the twist in degrees which it was necessary to apply to the torsion head to bring the swinging arm back to its original position. In the fifth column is recorded the total force in dynes which would be necessary to give the observed twist if applied to the extremity of the arm. In the single-arc method the couple is due to three causes: (1) the pressure upon the pole, including convection effects; (2) the vertical component of the earth's magnetic field acting upon the current in the swinging arm; and (3) the electromagnetic effect of the rest of the circuit upon the current in the movable parts; hence it is necessary to separate out (1) from (2) and (3). (2) was eliminated by placing the fixed pole first upon the east and then upon the west side of the suspended pole, and taking the mean of the observations. [The actual manner in which the reduction was done is shown by diagram 1, which however refers to the iron arc when the suspended pole was negative; the circles and crosses represent the readings for different currents when the anode was respectively on the east and west of the suspended pole.] In column 6 are recorded the ordinates



of the mean curve, and they indicate the force corrected for the earth's magnetic field. Reference to the earlier work upon the carbon arc will reveal how the correction was calculated for (3), the electromagnetic influence of the rest of the circuit upon the swinging arm, and column 7 contains the value of the pressure upon the pole corrected for this effect also.

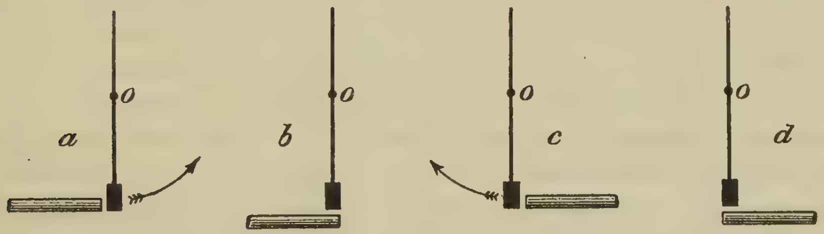
Table II is self-explanatory; it deals with Davis's observations and notes upon them. In both Tables typical results only are given; numerical values may be obtained in other cases from the diagrams.

Table II.—Silver Arc. Observer, Mr. Davis.

Double Arc Method.—Owing to vigorous melting, no definite result could be obtained, but the following was indicated:—

Current.	Volts.	Arc length.	Pressure upon anode.
4 amps.	26	3 mm.	$>0{\cdot}6$

Compensated Single Arc Method.—In the figure the movable parts are shown in plan. The copper rod is suspended centrally at 0, and provided with a silver pole-piece (shown in black). The other silver pole is shown in outline in different positions in different experiments.



The torsions were measured for dispositions *a* and *b* and also *c* and *d*; the difference between *a* and *b* and between *c* and *d* is a measure of the pressure upon the pole free from electromagnetic and earth effects.

Results for 3 mm. and 4 amp. arc.

Pole.	Type of arc.	Observed twist.	Torsion.	Pressure in dynes.
		°	°	
Anode	*c*	22	23	0·62
	d	45		
Cathode............	*a*	37	25	
	b	62		
	a	32	30	
			25°	0·68
Cathode............	*c*	85	32	
	d	53		
	c	65	12	

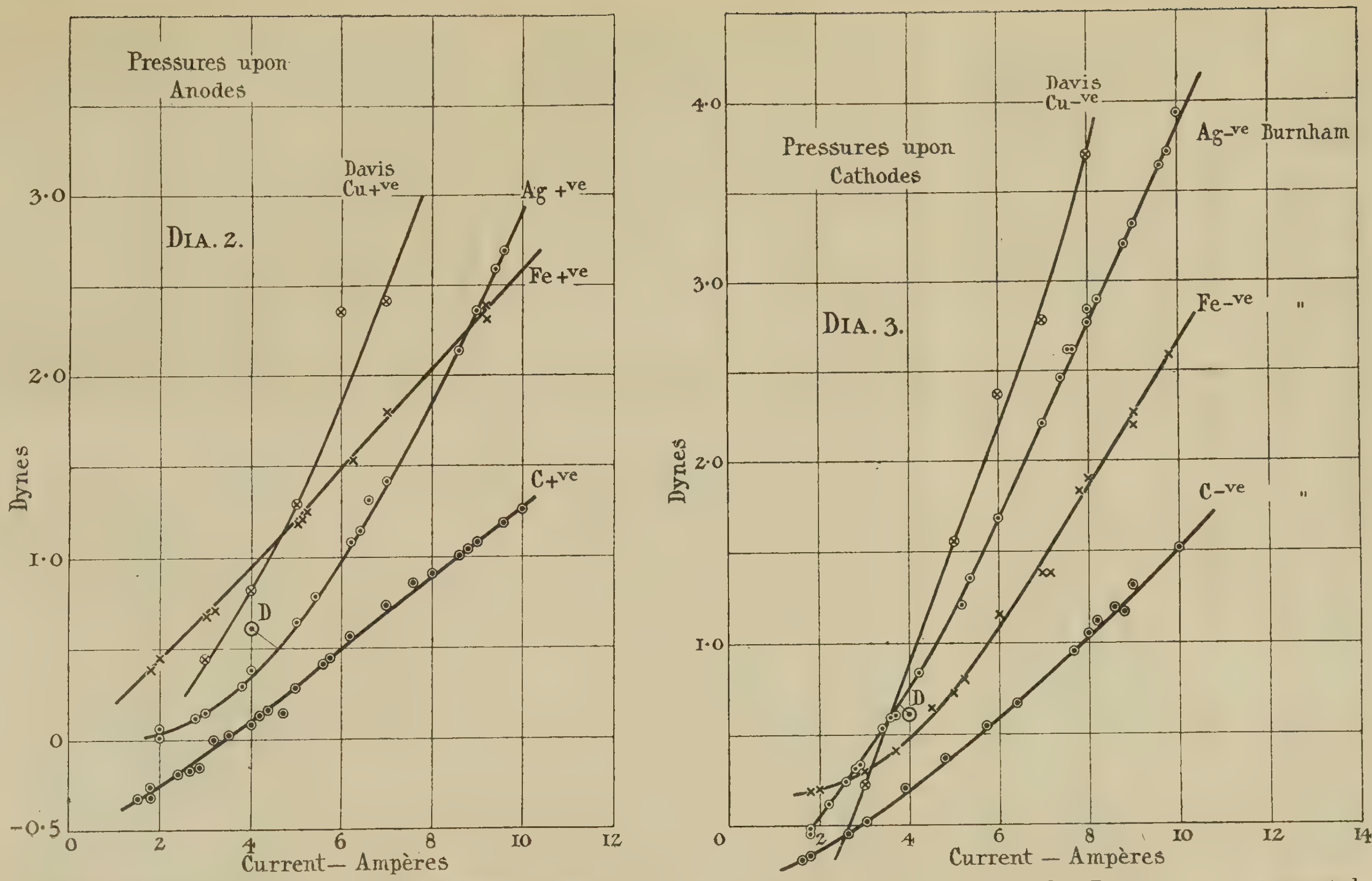
The Diagrams.

(a) *The Anode.*—Diagram 2 illustrates the results of the experiments upon copper, silver, and iron, as far as the pressures upon the anode are concerned. The curve for a carbon arc previously obtained by Mr. Burnham by the single-arc method is introduced for the purpose of comparison.

The curves have been corrected as far as possible for all extraneous influences, with the exception of convection currents. In each case, in which the single arc was used, a preliminary diagram like that reproduced in diagram 1 was drawn with the object of eliminating the effect of the earth's magnetic field; the amount of concordance between the individual readings is better gauged from that diagram than from diagram 2, since the latter gives only the mean smoothed curves obtained in the manner illustrated by diagram 1, after allowing for electromagnetic effects.

It was shown in the discussion of the carbon arc experiments that it was probable that an approximate correction for convection currents could be obtained by taking the zero for the ordinates where the straight part of the curve produced backwards met the vertical axis. The convection currents will not be the same in the case of all the arcs investigated, and if the above procedure be followed we shall add to the observed anode pressures 0·65 dyne for carbon, 2·0 dynes for silver, 0·2 dyne for iron, 2·0 dynes for copper. I am not entirely satisfied with this, but as the effects of convection amounts become less important in the case of metallic arcs where the reaction is large, the error is not likely to be serious. We note from diagram 2 that all the metallic arcs show greater pressures than the carbon arc. For small currents the greatest pressure is associated with the iron arc, but at higher current strengths the pressure upon the copper anode is the greatest, at 10 ampères the order being copper, silver, iron, and carbon. Copper, iron, and carbon exhibit a more nearly linear relationship than silver.

(b) *The Cathode.*—In diagram 3 are collected the cathode pressures for the four elements and again it appears that they are in the order copper, silver, iron, and carbon for currents above 3·5 ampères, below that value there is some uncertainty. In confirmation of the high value for the copper arc we find some early preliminary observations of Burnham's which give approximately 2·5 dynes as the mean value of anode and cathode pressures at 6 ampères. These curves also differ in shape, the graph for the iron cathode being less linear than the others, but since the correction for convection currents involves a straightening of the curves, as in the case of the carbon arc, it is considered that, if this correction could be made, they would not show an appreciable departure from a linear relationship, except in



Curves for silver, iron and carbon by the single-arc method; curve for copper by the double-arc method. Pressures are not corrected for convection effects. The observation marked D was obtained for silver by the double-arc method.

the case of the iron arc. By prolonging the straight parts of the curves back to the pressure axis the corrections are found to be as follows:—for carbon 0·85 dyne, iron 1·3 dyne, silver 1·6 dyne, copper 2·0 dynes.

DISCUSSION OF RESULTS. By Prof. W. G. DUFFIELD.

The Nature of the Particles responsible for the Reaction.

In the discussion of the carbon arc experiments, reasons were given for attributing the pressure to a recoil, and careful attention was directed to the nature of the particles whose expulsion occasioned the measured force. For the argument the earlier paper should be consulted: briefly the following considerations were in favour of the view that the particles were electrons and not carbon atoms:—

1. The value of e/m, calculated upon certain assumptions which appear legitimate, was of the order of magnitude associated with the electron.

2. The recoil diminished with increasing arc length, whereas the loss of carbon from the poles increased very greatly with the arc length.

3. If a recoil due to atomic expulsion were possible, it would have been 50 to 100 times greater than that observed.

Unfortunately we do not possess the data concerning the drop of potential across the cathode pole faces of metallic arcs, which are necessary for the evaluation of e/m in the present experiments; but, making the very rough assumption that they are half the total P.Ds. between the poles, we obtain from the formula $e/m = \mathrm{V}c^2/2p^2$. The values $2·8 \times 10^7$, $2·9 \times 10^7$, and $5·8 \times 10^7$ for copper, silver, and iron respectively, which are of the order of magnitude associated with the electron rather than with the atom.

It is of interest here to refer to a recent investigation whose object was to test whether the expulsion of molecules in the ordinary process of evaporation into the free atmosphere occasions a measurable reaction. While it indicates that the arc recoil is not likely to be due to the projection of uncharged molecules, it raises another interesting question. Several methods were employed, amongst others water was boiled on the pan of a balance, and an apparatus in the form of Hero's engine was used in which the sum of the areas of the apertures was equal to that of the evaporating surface, but in neither case was any recoil observed; this is because the ejected molecules push aside those of the atmosphere and prevent them from communicating their momenta to the surface. If, therefore, we agree that the ejection of electrons does cause a recoil, it remains to argue why they should be capable of this. In view of the ionisation in the arc, we can hardly presume that the electrons go through without touching the molecules, so the probability is that the original electron's momentum is passed on from atom to atom and that we may regard the atoms as stepping-stones for the electrons in their track across the arc.

It is worth noting here that it appears probable that, if evaporation could be produced at such a rate that the number of vapour molecules expelled per second exceeds twice the number directed towards the surface from above, an excess pressure would be obtained. Calculation shows that this rate of evaporation might be reached in the carbon arc if the total amount of carbon lost from the cathode in a 10-ampère arc were confined to an area of 1/63 sq. mm. on that pole, but as the area of the bright spot is obviously considerably larger than 1 sq. mm.,* and as it is known that 66 per cent. of the loss occurs from the hot contour of the carbon, this is not favourable to the view that the recoil is due to molecular expulsion.

Relation between Electronic and Atomic Properties.

If we accept the view that the projection in metallic arcs is electronic it becomes a matter of great interest to enquire whether there is any evident relation between the mechanical properties of the ejected electrons and of the atoms composing the poles—between their momenta or their kinetic energies, for example. If, as is generally accepted, the temperature of the poles of an arc corresponds to the boiling point of the material composing them, we may assume that the average kinetic energy of the molecules at the pole-face is equal to that of the neighbouring air molecules. Thus, the molecular velocity of the material of the poles (molecular weight = M) at the temperature of the melting pole (T° absolute) is given by

$V = V_0^H \sqrt{(2/273)}\sqrt{(T/M)}$, where V_0^H is the velocity of the hydrogen molecule at 0° C.,

hence $V = a\sqrt{(T/M)}$, where $a = 1{\cdot}58 \times 10^4$.

The molecular momentum, at the same temperature, is given by $HMV = b\sqrt{(T.M.)}$, where $b = 2{\cdot}6 \times 10^{-20}$ and H is the mass of the hydrogen atom.

The kinetic energy of the molecule is $\frac{1}{2}MV^2H$ or $\frac{1}{2}a^2HT$, which is equal to $2{\cdot}05 \times 10^{-16}$ T; this is independent of the number of atoms in the molecule.

From the observed reaction pressure at 10 ampères we can calculate the momentum and the kinetic energy of the electron. Since the number of electronic charges, *n*, equivalent to the passage of 10 coulombs between the poles is $6{\cdot}3 \times 10^{19}$, we obtain the momentum associated with each electron by dividing the observed recoil by this quantity. By further dividing this by the mass of the electron we obtain the velocity with which it leaves the pole. This is on the assumption that all the current is electron-borne: but if, instead of n charges, αn are carried by electrons from the cathode and the remainder of the current is carried by positively charged molecules moving in the opposite direction, this velocity must be multiplied by $1/\alpha$.

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* It is 3 sq. mm. according to Reich's formula, 'Phys. Zeitschr.,' vol. 7, p. 73 (1906).

The loss of momentum from the cathode is αnmv in 1 second, and this must be balanced by the pressure P applied through the torsion of the suspension. If the electrons are emitted normal to a hemispherical pole face, which is not very different from random projection from a small area of a flat pole face, we have $\alpha nmv = 2\mathrm{P}$, whence the electronic momentum $= mv = 2\mathrm{P}/\alpha n$, and the electronic velocity $= v = 2\mathrm{P}/m\alpha n$. The electronic energy $= \frac{1}{2} mv^2 = 2\mathrm{P}^2/m\alpha^2 n^2$.

In Tables III and IV are set forth the momenta and energies of molecules and electrons calculated in this way for $\alpha = 1$ and $\alpha = 1/2$.

If, instead of being monatomic, the vapour molecule comprises two, three, or four atoms, the above molecular velocities are to be divided by $\sqrt{(2)}$, $\sqrt{(3)}$, or $\sqrt{(4)}$, and the molecular momenta to be multiplied by the same quantities. The molecular kinetic energies remain unaffected. If the electronic emission were always normal to the pole face, the electronic energies above should be divided by 4, thereby improving the agreement with molecular energies.

It appears that the molecular momenta are too high, and their energies too low, for good agreement with similar electronic quantities. But the discordances are not such as to be inconsistent with the view that the phenomenon is of a photo-electric or thermionic character, the "free" electrons sharing in the heat energy of the poles in the manner discussed by Richardson. Since the electronic energies are consistently greater than the molecular energies, there is some suspicion that the energies may be shared according to the quantum, rather than the equipartition, theory, which would seem to indicate that, before escaping, the electrons rotate in orbits about the atoms.

The Nature of the Electronic Discharge.

The electron velocities yielded by this investigation are of the order of magnitude associated with other modes of electronic projection. It seems established that different atoms eject them with different velocities in the arc, and it appears that, though there is no simple connection between the velocities and the atomic weights or atomic numbers, it is in general true that the heavier elements emit them with greater velocities than carbon does. This suggests that the velocity may be an atomic property rather than a property of the incident light; the instability occasioning the projection arising, perhaps, from the access of electrons from the source of current

Table III.

Element.	Molecules.				P dynes.	Electrons.				Ratio MV/*mv*.	
	Atomic weight.	B. point, ° Abs.	V.	MV.		$\alpha = 1$ *v*.	$\alpha = \frac{1}{2}$ *v*.	$\alpha = 1$ *mv*.	$\alpha = \frac{1}{2}$ *mv*.	$\alpha = 1$.	$\alpha = \frac{1}{2}$.
Copper	64	2580	1·00 × 10^{5}	1·06 × 10^{-17}	5·9	2·14 × 10^{8}	4·28 × 10^{8}	1·88 × 10^{-19}	3·76 × 10^{-19}	57	28
Silver...............	108	2228	0·72	1·28	4·3	1·54	3·08	1·36	2·72	94	47
Iron	56	2723	1·1	1·04	3·2	1·16	2·32	1·02	2·04	102	51
Carbon	12	4000*	2·9	0·56	2·0	0·72	1·44	0·64	1·28	95	48
									Means	86	43

* Waidner and Burgess, Bureau of Standards, Washington, 1904.

Table IV.

Element.	Molecular energy.	Electronic Energies.		Ratio Molecular/Electronic Energies.	
		$\alpha = 1$.	$\alpha = \frac{1}{2}$.	$\alpha = 1$.	$\alpha = \frac{1}{2}$.
Copper	0·53 × 10^{-12}	2·02 × 10^{-11}	8·08 × 10^{-11}	1/37	1/153
Silver	0·46	1·04	4·16	1/23	1/90
Iron	0·56	0·59	2·36	1/10·5	1/42
Carbon	0·82	0·23	0·92	1/2·8	1/11

supply. But, on the other hand, as we have said, the phenomenon is not obviously inconsistent with the view that it is of a photo-electric or thermionic character. The inconsistency might be less if we knew the proportion of current electron-borne and the distribution of the projected electrons about the axis of the arc.

In favour of the phenomenon being thermionic, we have the fact that, in order to maintain an arc, it is necessary to keep the cathode temperature high; moving the carbons so that a fresh portion is substituted for the hot cathode, the arc at once goes out.

On the other hand, if we regard the phenomenon as photo-electric and calculate the mean wave-length of the light, which is effective in promoting the emission, from the equation $h(\nu-\nu_0) = \frac{1}{2}mv^2$, we find the following values, taking the threshold wave-lengths for copper and carbon as 3090 and 2600 Å.U. respectively:—

For $\alpha = 1$, $\lambda = 740$ Å.U. for copper, 2000 Å.U. for carbon.
For $\alpha = 1/2$, $\lambda = 226$ Å.U. for copper, 1700 Å.U. for carbon.

The values for copper represent light far in the ultra-violet, but it may be that they are possible values, since the question of the light penetrating from the vapour to the poles can scarcely arise in the arc. The carbon results are quite satisfactory in this respect, but, on the whole, the evidence is not fully in accord with the photo-electric explanation of the emission.

The possibility that "polar lines" in arc spectra are due to the same action as that which occasions the electronic emission has been discussed by the writer in the earlier paper upon the carbon arc, where copper and iron lines also received attention.

As regards the choice of the value of α, it was found in the case of the carbon arc, that the phenomenon appeared to be more in accord with the hypothesis that, at the cathode, half only of the current was carried by electrons, the remainder being carried by positively charged ions moving towards it. As the chemical interactions become important in this respect, and as little is known about them in metallic arcs, we must await further evidence before making a choice. The probability is that, if α is not equal to unity, it is a simple fraction. It may vary with the nature of the metal.

The above discussion naturally reopens the question whether the phenomenon of boiling may not be connected with the energy necessary to expel an electron from the atom or from the surface of the evaporating metal. The present research certainly suggests that some such connection exists in the special circumstances under which a metal is vapourised in the arc, but there does not seem to be any other evidence which indicates that the same holds good under normal conditions of boiling.

The Mechanism whereby a Gas may be Heated by Radiation.

The hypothesis of atomic or molecular motions arising from electronic projection is worthy of close examination. The mechanism whereby the addition of radiant heat to a gas increases the energy of translation of its molecules remains obscure, but if the radiation falling upon an atom is such that it can cause the ejection of an electron by some such process as photo-electric action, we can picture one means whereby the velocity of the atom may be increased, and the gas therefore heated; the amount should be calculable if the energy of the electron is known. If there is none of the type of radiation in the incident beam which the gas is capable of absorbing, it will not be heated—unless light-pressure is, under these conditions, capable of producing an effect upon the velocity of the atom.

Presumably, any radiation which is absorbed is absorbed at the frequency represented by an absorption band in the gas or vapour, and we should look for ionisation when absorption accompanied by heating occurs. There may be another type of absorption which occurs without ionisation and which may be called resonance absorption; it would be expected to be unaccompanied by rise of temperature, but it would be interesting to test this point experimentally. In the ionisation type of absorption, which we should expect to find more particularly in ultra-violet regions, the electron shot off may either strike a neutral atom and cause it also to participate in the heat motion, or it may meet a charged atom and enter it, in which case it will cause it to emit precisely that type of radiation which it originally absorbed from the incident beam; this may be the origin of "scattering." The total kinetic energy of the affected atoms is ultimately of course equal to the radiant energy which has disappeared.

Assuming Newtonian mechanics, we may calculate the order of the number of molecules affected:—

The amount of energy necessary to raise the temperature of one gas molecule through 1° C. is given on p. 333 as $2{\cdot}05 \times 10^{-16}$ ergs, whereas the energy of a projected electron is of the order of 5×10^{-12} ergs (this is nearly the value for iron), hence the emission of one electron with a velocity of about 10^8 cm. per second will provide sufficient energy to raise the temperature of 25,000 molecules through 1° C.

The absence of heating when X-rays are passed through a gas is due to the small percentage of molecules which are ionized, only about 1 in 10^{12} being affected. The usual absence of observed ionization when a stream of radiant energy is passed through a gas is probably due to the small amount of absorption, as it is notoriously difficult to heat a gas by such means. The upper layers of the atmosphere are, however, ionized by solar radiation, and it is possible that the temperature inversion which is frequently observed in the upper regions of the stratosphere is partly due to the consequent heating.

Evidence of another character is afforded by the experiments of Wood and Rayleigh upon the nature of the scattered light in an absorption band. The former showed that there is complete absence of polarization in the light scattered from the centre of the band, and the latter added the fact that the light scattered from the wings of the band showed increasing amounts of polarisation as the distance from the centre increased. The interpretation may well be that the central scattering is of the nature described above, which would obviously not be polarized, but that the wing scattering may be of the reflected character, when the polarisation is the result of geometric considerations.

An interesting statement, which lends support to the above view of the mechanism whereby a gas is heated is given by Lewis* in the following words:—"Hughes has found that the ionisation of air sets in at a wave-length of 1350 Å.U. This is likewise the position of the *absorption* band of oxygen in the ultra-violet. We may conclude, therefore, that the effect in air is due to the ionisation of oxygen, and hence we should be able to calculate the ionisation potential of oxygen from the expression $V = h\nu/e$. The value of V thus obtained is 9·2 volts, which is identical with the observed value."

The matter is one of extreme interest, and is the subject of further investigation in the writer's laboratory.

Anomalous Effect in the Iron Arc.

It was observed by Burnham, in his experiments with the iron arc, that the formation of a turbulent drop of molten iron upon the pole increased the pressure very greatly. Davis subsequently tested this point carefully, conducting experiments over a wide range of current strengths, and obtained values of the maximum pressures experienced by the poles; using the double-arc method, in which the supply of heat is greater than in the other, he found it almost impossible to obtain readings consistent with the low values given by the single-arc method, when the poles were less heated. The pressure appeared to be low at first, but as time went on and the molten drop formed, the pressures became steadily greater, maximum values being obtained just before the molten drop fell off, when the arc was roaring violently. It is clear from diagrams 4 and 5 that, under these special conditions, the pressure is increased enormously, being at 10 ampères, roughly seven times greater than that previously measured for the iron arc. The excellent agreement between the observations of the two observers for the molten poles is very satisfactory considering the difficulty of the experiments. The relationship between the pressure and the current is linear for anode pressures, but for those upon the cathode nearly parabolic. Corrections have not been introduced for convection currents, but it is not considered that they would be large enough to modify the shape of the curve appreciably, as they do in the case of the normal curves (*vide* carbon arc paper).

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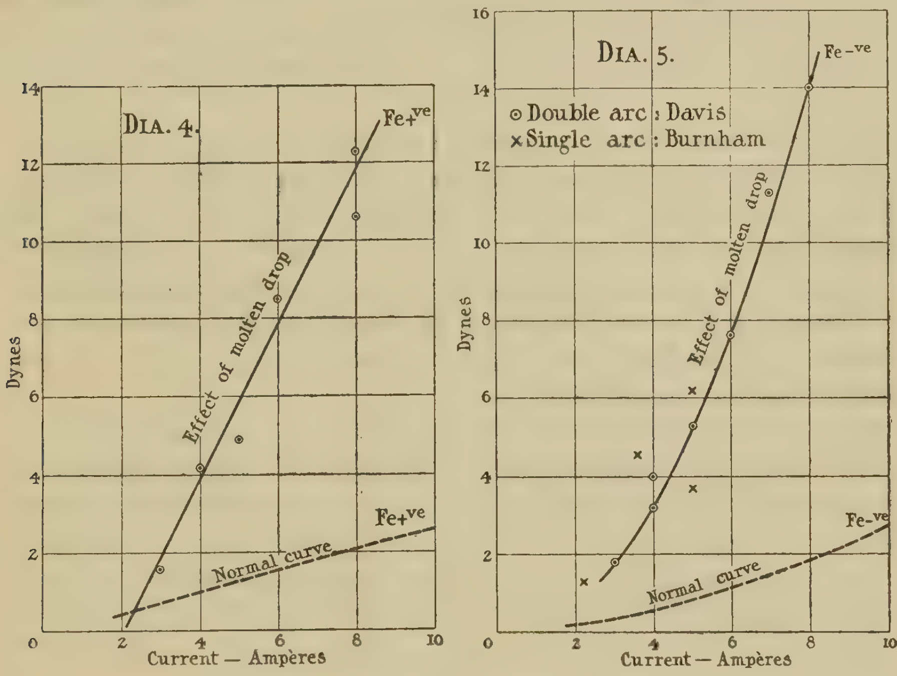
* Lewis, 'A System of Physical Chemistry,' vol. 3, p. 129.



Curves not corrected for convection effects.

It was noticed that the arc was more like a narrow divergent jet when it sprang from a molten patch.

As the measurements made at widely different times by the two observers are in excellent agreement, it does not seem that the size of the drop is of paramount importance, but experiments designed to test this point directly were not made.

A careful study of the appearance of a horizontal iron arc in the quiescent and turbulent states was made by the writer with the help of Lieutenant Helsby. An image of the arc was focussed upon a ruled screen, and the arc length and current kept constant. A molten drop appeared first upon the anode, but there seemed to be a molten film upon the cathode at all times, even though it did not at first collect into a drop; this may, however, have been an optical effect. When very narrow poles were used, the heating was more intense, and the drops more rapidly developed. When rounded drops appeared on both poles the turbulent state ensued and the arc became noisy.

The drops were seldom spherical, but appeared to be subjected to a pressure which flattened them considerably, this may be additional evidence of the pressure within the arc, but is possibly a surface tension effect. The deformation was more noticeable on some occasions than on others, and it is believed that there was then a bubble of gas within the molten mass. On stopping the current, the deformed drop frequently swelled out to a spherical shape, sometimes bursting and emitting the gas within. It then solidified, leaving a crater behind it.

Some of the ends were knocked off and found to contain cavities, the curious thing about them being that they were not always spherical but often deformed like the outer surface of the drop, as though by pressure along the axis of the arc. These were usually rather deep down (1 mm. to 2 mm.) below the spot from which the arc sprang; the material surrounding them must have solidified while the arc was still running, and as the drop grew in size by the melting of more iron, they gradually receded from the great source of heat.

The potential difference between the poles increased slightly when the arc passed from the quiescent to the turbulent state, the amount being about 4 volts. Experiments with fixed poles were necessary to discover this difference.

The only suggestion the writer can make to account for this anomalous value of the pressure in the iron arc is that the rate of molecular projection so increased that a larger number of molecules left unit area of the surface of the pole than twice the number of molecules directed towards the surface from without, in which case, as we have seen (p. 333), a recoil due to molecular projection might be occasioned. This receives some support from the smallness of the area from which the turbulent iron arc springs, but this explanation is not put forward with complete conviction.

It is interesting to note that Hagenbach and Veillon* claim to have found six different forms of the copper arc, that there are three different potential drops which may occur at the anode, and that with each of these it is possible to have two different cathode potential drops; these may be related to the different ionisation potentials associated with any one element. They observed similar variations with other metallic arcs.

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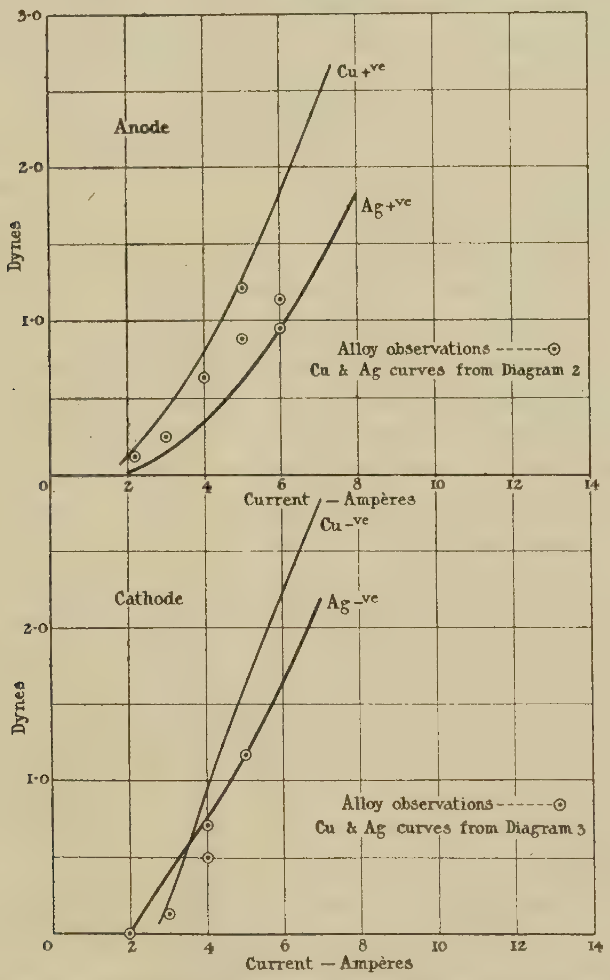
* Hagenback and Veillon, 'Phys. Zeitschr.,' vol. 12, p. 1015 (1911).

Experiments with an Alloy.

A test was made with an alloy composed of 80 per cent. silver and 20 per cent. copper in the usual way, both poles being of the same composition. The results are given in diagram 6.

DIAGRAM 6.



Pressure upon the poles of an alloy of 80 per cent. silver, 20 per cent. copper.

When the suspended pole was positive, the pressure upon it was intermediate between the pressures measured for copper and silver when tested separately. These results are consistent with the photo-electric view of the phenomenon, since Hughes states that with alloys the photo-electric effect is intermediate between the effects of the constituent metals and varies linearly with the amount of either.

When the suspended pole was negative, the pressures approximated more closely to those observed when the poles were of pure silver, the effect of the copper being, if anything, to reduce the pressure, as would be expected at low current strengths.

Composite Arcs.

Under this heading we include the study of arcs in which the positive pole was of different material from that composing the negative pole. Burnham made an extended examination of the silver-carbon arc, using each pole in turn as anode and cathode, and testing the recoil under current strengths ranging from 2 to 10 ampères. Davis, using the difficult double arc method, measured the pressure experienced by the poles of a copper-carbon arc of 3 mm. length and 5 ampères current.

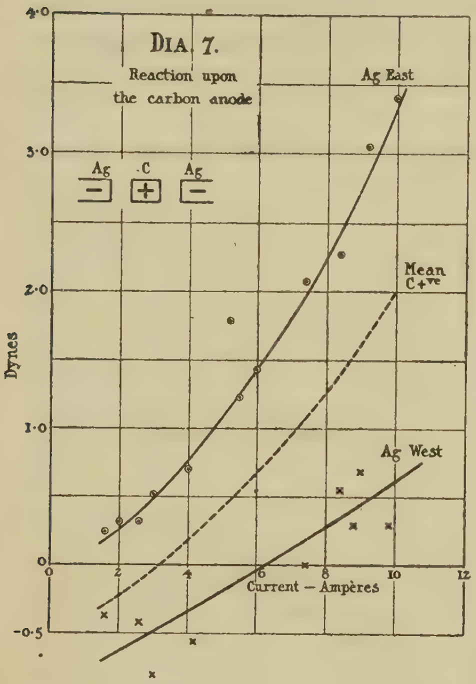
Using the uncompensated single arc method, the results shown in diagrams 7, 8, 9, and 10 were obtained, the top and bottom curves being drawn for the east and west positions of the fixed pole, corrections for the electromagnetic effect of the rest of the circuit having previously been made. The mean curve gives the result corrected for the influence of the earth's magnetic field. It will be noticed that the curves are divergent when the anode was being tested, whether of silver or carbon, but more nearly parallel or even convergent when the suspended pole was the cathode. The reason for this has not been discovered.

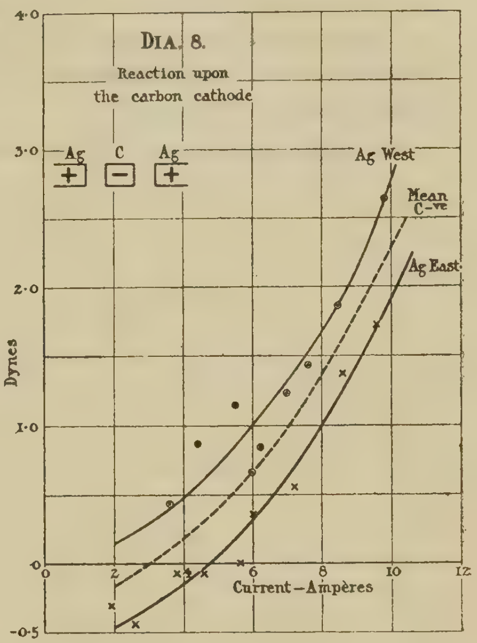
In diagram 11 are shown the values thus obtained for the anodes side by side with those given by arcs in which both poles were of the same metal. The highest values were obtained when both electrodes were of silver, the lowest when both were of carbon. The substitution of a carbon cathode in the silver arc led to a reduction in the recoil as high values of the current were reached, though up to 4 ampères the curves are practically coincident.

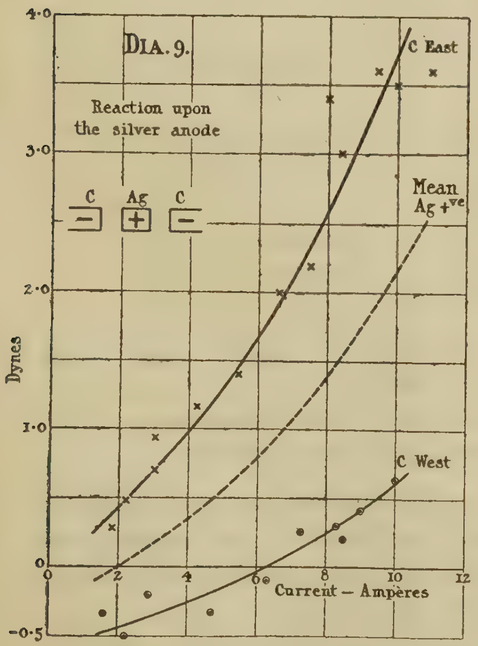
Similarly, substituting silver for the cathode in a pure carbon arc led to an increase in the recoil, which became more pronounced as the current strength increased.

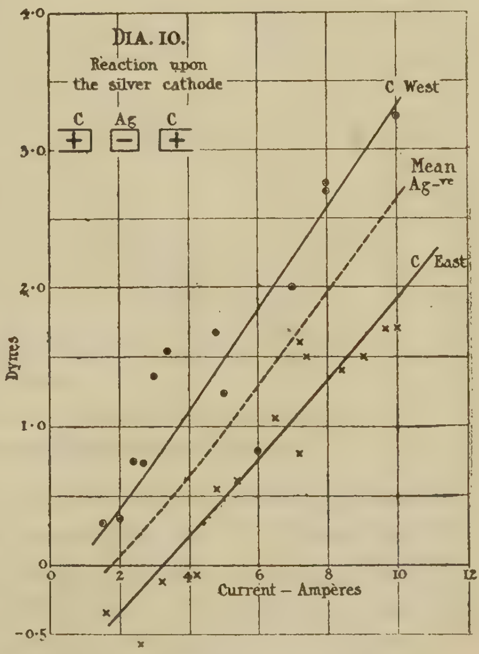
The effect of changing the cathode is to alter the recoil upon the anode in accordance with the tendency of the material of the cathode, when used alone, to give a high or a low pressure within the arc.

Similar results were obtained when the suspended pole was the cathode and the anode changed from silver to carbon:—Diagram 12 shows that, when the cathode was of silver, the effects obtained with a silver and a carbon anode were nearly equal up to 4 ampères, but that, at larger current strengths, the carbon anode gave results very much lower than those obtained with a silver-silver arc. Also, the substitution of silver for the anode in a carbon-carbon arc effected an increase of pressure, which was





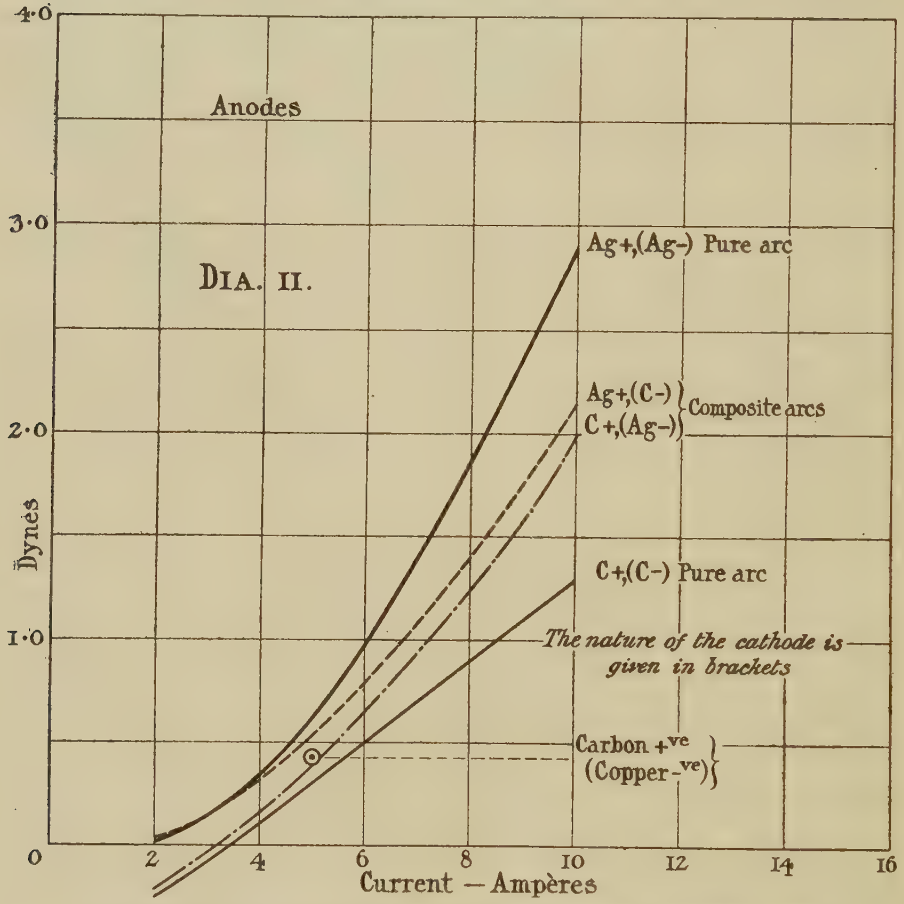




Composite Arcs.
Pressures upon the poles of a silver-carbon arc.

very marked at 10 ampères. In all cases the pressure was chiefly determined by the material constituting the suspended pole, the nature of the other exerting a secondary influence which became increasingly important as the current strength increased.

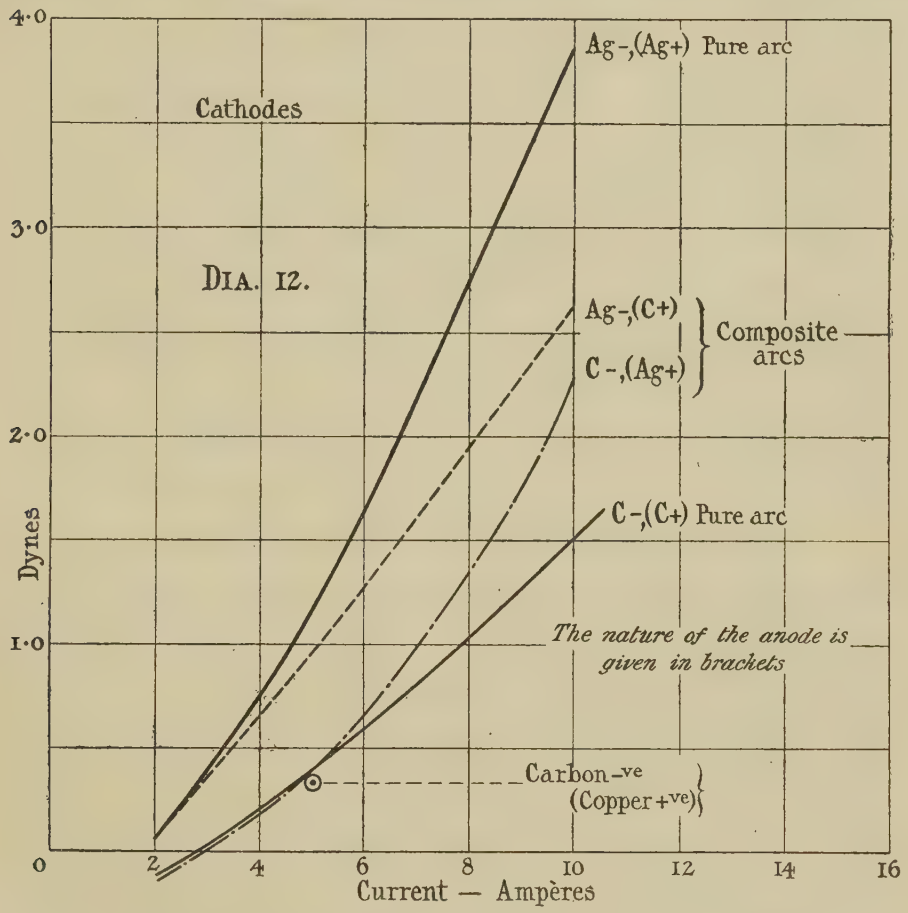
The only suggestion which can be made to account for this is that there is



Comparison of the pressures upon the poles of pure and composite arcs. The circle shows a single observation upon a copper-carbon arc.

transfer of material between the poles and a certain amount of condensation of the material of either pole upon the other, and that the contaminated poles behave as though they were an alloy or a mixture of the two metals. Deposition of this sort has been observed by the writer.

We have always insisted upon the important part played by the nature of the gas or vapour between the poles, and its chemical reaction with the material of the poles; it is possible that these interactions are modified as the arc space becomes impregnated with the vapour of a foreign element and that there is a change in the proportion of the current which is atom borne. The greater the number of electrons carrying the current, the greater the recoil pressure.



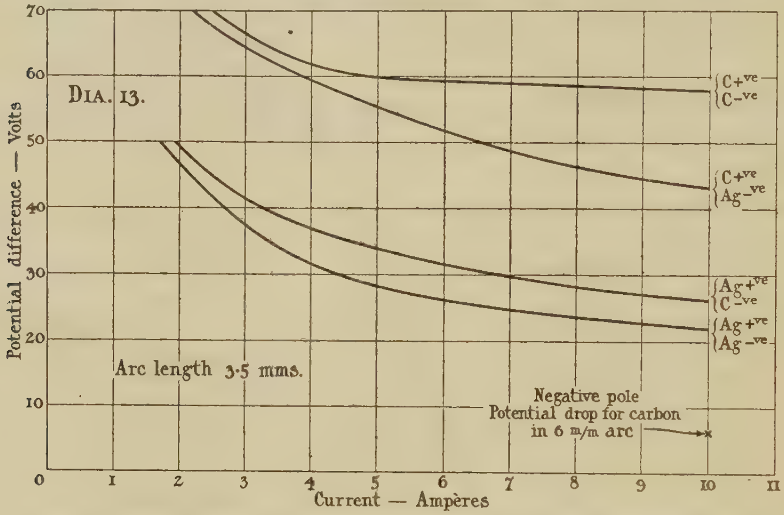
Comparison of the pressures upon the poles of pure and composite arcs. The circle shows a single observation upon a copper-carbon arc.

The Potential Difference between the Poles when the Material of One is Varied.

Diagram 13 has been drawn from the observations already quoted. It shows the variation of the potential difference between the poles when arcs of carbon-carbon, carbon-silver, and silver-silver were employed under different conditions of current strength. The individual observations have been omitted, and only the mean curves shown.

Altering the nature of the anode has a much greater effect upon the P.D.

than altering the cathode, thus:—altering the anode from silver to carbon when the cathode is silver increases the P.D. by 21 volts, whereas altering the cathode from silver to carbon when the anode is silver, increases the P.D. by only 4 volts. Also, altering the anode from silver to carbon when the cathode is carbon, increases the P.D. by 32 volts, whereas altering the cathode from silver to carbon when the anode is carbon, increases the P.D. by 15 volts. These values are for a current of 10 ampères.



The potential difference between the poles of pure and composite arcs.

The dependence of the P.D. upon the nature of the anode is partly concerned with the projection of electrons from that pole against the current, which acts as a back E.M.F. at the anode surface. We have previously instanced a case in which the P.D. of a carbon arc was reduced by diminishing the heating of the anode, which was accomplished by substituting a rotating carbon surface for the fixed pole.* The increase in the P.D. consequent upon the substitution of carbon for a metal, is due to the readiness with which electrons are emitted from a hot carbon surface.

Comparing diagrams 11, 12, and 13, it is interesting to note that the lowest recoil pressure is given with the carbon-carbon arc, which requires the highest potential difference between the terminals, and that the highest pressure, given by the silver-silver arc, is associated with the smallest potential difference; also, that the substitution of carbon for silver increases the total potential difference, but diminishes the recoil upon each pole. The equation relating the recoil pressure to the potential drop outwards across the pole face requires that the former should be proportional to the square root of the latter (*vide* earlier paper); it is important, therefore, to emphasise that, as Duddell showed, the potential drop across the cathode pole face is only one item, and by no means the largest, in the aggregate which constitutes the total P.D. between the poles.

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* Duffield and Waller, 'Roy. Soc. Proc.,' A, vol. 92, p. 247 (1916).

[*Supplementary note added April* 20, 1920.—*W. G. D.*—As it may not at once be obvious that a pressure upon the poles is not to be expected from the motion of ions arising solely from the electrostatic forces within the arc, it may be useful to deal briefly with this point.

An ion starting from rest with a charge e in an electric field R, supposed uniform, exerts a pull upon the pole of opposite sign equal to $\mathrm{R}e$. If it falls freely for a time, t, the velocity with which it strikes the pole is $\mathrm{R}et/m$, and the rate of change of the momentum delivered to the electrode $= \mathrm{R}et/m \times m/t = \mathrm{R}e$. Consequently, for ions starting from rest and attaining a velocity solely on account of the electric field in which it finds itself, it follows that there is a balance between the effect of the electrostatic force and the rate of change of momentum delivered to the pole.

In particular, we should not expect any additional pressure upon the anode due to the bombardment of negative ions whose motion arises solely from the attraction of that pole. Further, at the anode electronic projection may be intense on account of the high temperature, but, since the electrons are brought to rest at a short distance from the pole face by the electrostatic forces, these contribute nothing to the reaction, the initial recoil being balanced by the attraction of the pole between the instants of projection and of their being brought to rest.

At the cathode the conditions are different—the electronic projection there occasions a reaction which is not balanced by any attraction between that pole and the electron.

I think that, in view of the above considerations, we may safely rule out of account the possibility of any considerable part of the observed effect being due to anything in the nature of the so-called "electric wind," and it appears that the possible sources of pressure upon the poles are considerably narrowed. This is supported by the observation mentioned in the earlier paper, that a reaction was observed upon the cathode in an highly exhausted vacuum tube.

Another point to which attention may be drawn is that, though it is possible to conceive an *isolated* hot pole, though ejecting torrents of electrons, being in equilibrium with the surrounding atmosphere, there is good reason to expect its equilibrium to be disturbed if it is connected to the negative terminal of a source of current supply and the positive terminal brought near it, that is to say, if we pass from the condition of a hot body emitting thermionically to the conditions in an arc—it is known that some of the projected electrons (either isolated or attached to atoms to form negative ions) get across to the positive pole, since this is the means whereby current is transported, and it seems inevitable that this stream of material particles (if electrons can be called material) represents a stream of momentum outwards from the cathode; as this stream only ceases when it meets the anode, we expect to find an equal reaction upon that pole. Remembering that the momentum given up to that pole is unaffected by the electrostatic forces encountered by the ions moving freely within the arc, as we have just shown, the only reason why we may find unequal pressures upon the poles lies in the efficacy of convection currents to sweep a fraction of the momentum out of the arc.

This is, I think, a point of some interest; as long as the ultimate reaction of the electrons projected from the cathode is directed against air molecules, we may have equilibrium (as there is in a radiometer tube when the gas pressure is high), but, with the flow of the electric current, their momentum is only finally discharged against the solid anode, so that there is an unbalanced stream of momentum from the cathode (as there is in a radiometer tube sufficiently exhausted for the hot gas molecules to strike the sides of the vessel); this it is which gives rise to the observed reaction.

It is to be remarked that light pressure does not seem to be responsible for the observed effect, unless we regard photo-electric action due to the incidence of light waves as included under this head, because we should expect to find the greatest pressure upon the carbon poles, both because the temperature is higher than in the case of metallic arcs, and the power consumed by it for a given current is far the largest. On the whole, though in so complicated a phenomenon as the electric arc, it would be vain to attempt to speak with conviction, I think that, though there are still difficulties, the balance of evidence favours electronic projection from the cathode as responsible for the recoil usually observed. Radiometer action and evaporation of molecules have been dealt with previously, and found to be improbable.]

The interest taken by Prof. O. W. Richardson in this research has been a stimulus to the writer responsible for the theoretical discussion, which he very gratefully acknowledges. Mr. A. H. Davis was in receipt of a grant from the Committee of the Privy Council for Scientific and Industrial Research, to whom the thanks of the authors are accorded.

Some Notes on Krypton and Xenon.

By J. N. Collie, F.R.S.

(Received April 6, 1920.)

During some experiments that were made with krypton and xenon in vacuum tubes it was noticed that in the red end of the spectrum there were lines that had not been measured. Attempts were therefore made to photograph them, but without success, and their wave-lengths were determined instead by two Hilger spectroscopes, one an ordinary prism instrument and the other a glass grating instrument. The readings, therefore, do not claim any great degree of accuracy, but as they are the mean of a large number of readings, and of two instruments, they cannot be very inaccurate. Moreover, the spectroscopes were carefully standardised by all the red neon and argon lines occurring in the same part of the spectrum. The lines produced both by the ordinary discharge and also by the Leyden jar discharge were measured.

The intensities of the lines varied with different tubes, the numbers given are the mean values. In one xenon tube some of the lines were particularly bright. This possibly was due to the pressure of the gas being exactly favourable for bringing out the lines. It was with the Leyden jar discharge that this was noticed. The brilliant lines were the following:—6880 (5), 6730 (5), 6669 (5), 6470 (7), 6318 (8), 6179 (8).

Mention may also be made that in the krypton spectrum with the Leyden jar discharge, there were a very large number of extremely faint lines between those of wave-length 6421 and 5994. Only the more prominent ones have been measured.

Whilst these experiments with xenon were being carried out a peculiar phenomenon was noticed, namely, that when heavy currents, from a large coil with a platinum break, were passed through tubes containing xenon, the gas rapidly disappeared and the tube became vacuous. At the same time the tubes became heavily blackened, owing to the splashed metal from the electrode. This splashing of the metal from the cathode is much more marked with some gases than with others; but tubes containing the gases argon, krypton, and xenon, seem to blacken more readily than those containing other gases. Xenon, however, allows the metal of the cathode to be thrown off more easily than any other gas.

It has already been pointed out,* that when vacuum tubes, containing the rare gases in a state of perfect purity, have a moderately strong discharge

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* 'Roy. Soc. Proc.,' A, vol. 95, p. 115 (1918).

Xenon, ordinary spectrum.	Xenon, Leyden jar spectrum.	Krypton, ordinary spectrum.	Krypton, Leyden jar spectrum.
7121 (2)	*7121 (1)	7595 (4)	6768 (1)
6972 (1)	6994 (2)	6907 (2)	*6701 (1)
6925 (1)	*6880 (2)	6815 (2)	*6662 (1)
6880 (3)	*6831 (1)	6701 (2)	6612 (1)
6871 (3)	6808 (3)	6662 (2)	*6574 (1)
6850 (1)	6793 (1)	6574 (1)	*6563 (10)
6831 (1)	*6730 (1)	6563 (10)	*6512 (4)
6780 (1)	6697 (2)	6550 (1)	*6456 (4)
6730 (1)	*6669 (2)	6536 (1)	*6421 (5)
6669 (2)	*6636 (1)	6512 (1)	6312 (2)
6636 (1)	6621 (1)	6498 (1)	6304 (2)
6610 (1)	*6597 (10)	6481 (1)	6302 (1)
6597 (3)	6529 (1)	6456 (7)	6204 (1)
6554 (1)	6513 (2)	6421 (7)	6170 (1)
6546 (1)	6506 (1)	6383 (1)	*6153 (1)
6535 (1)	*6501 (1)	6352 (1)	6121 (1)
6525 (1)	*6488 (1)	6236 (1)	6108 (1)
6503 (3)	*6470 (1)	6223 (1)	6097 (1)
6501 (3)	*6420 (1)	6153 (1)	6094 (1)
6488 (1)	6399 (1)	6083 (2)	*6083 (1)
6470 (1)	6377 (2)	6056 (3)	*6056 (2)
6452 (1)	*6357 (3)	6032 (1)	6038 (1)
6420 (1)	*6343 (3)	6012 (2)	6022 (1)
6357 (3)	*6318 (2)	5994 (2)	*6012 (2)
6343 (3)	6301 (2)		*5994 (3)
6333 (2)	*6292 (1)		5969 (1)
6318 (4)	*6285 (1)		5946 (1)
6292 (2)	6277 (3)		*5871 (5)
6285 (2)	6270 (3)		*5833 (1)
6260 (2)	*6260 (1)		*5827 (1)
6218 (1)	6241 (1)		5778 (1)
6201 (1)	6226 (1)		5771 (1)
6199 (1)	6208 (1)		5753 (1)
6193 (2)	*6199 (1)		5736 (1)
6179 (2)	*6193 (1)		*5718 (1)
	*6179 (2)		
	*6164 (1)		
	6146 (1)		
	6114 (1)		
	*6112 (1)		
	6102 (1)		
	6098 (4)		
	6051 (4)		
	6036 (4)		

The lines marked with a * are common to both spectra.

from a coil passed through them, even at pressures as high as 40 mm., cadmium could be easily volatilised from a cadmium cathode. But in one respect xenon differs from the other rare gases, for when a xenon tube becomes vacuous after heavy sparking only a very small portion of the xenon can be set free again by strongly heating the splashed metal. This is not the case with the other rare gases. Although they also become vacuous on long running, the whole of the gas that has disappeared can be recovered easily by heating the tubes.

That xenon should behave differently was curious, so further experiments were made with measured quantities of xenon, and with different metallic electrodes.

The first experiments were with ordinary vacuum tubes, with aluminium electrodes, and connected with a Töpler pump. The metallic splashing does not occur till the gas shows a clean spectrum, it then proceeds rapidly. In every case, after six or eight hours, the tubes showed a phosphorescent vacuum, even after heating the metallic splash to as high a temperature as the tubes would stand without collapsing.

The next set of experiments were made with the Merton apparatus that does away with all taps,* to which was fused on a hard glass tube containing magnesium, copper, copper oxide, and phosphorus pentoxide, also a small charcoal bulb. 1·05 c.c. pure xenon was put into the apparatus. The electrodes in the sparking tube were made of aluminium wire 3 mm. thick and 20 mm. long. At first the magnesium, copper, and copper oxide were heated for several hours so as to be quite sure the gas was pure. This was hardly necessary, as it gave a beautifully clean spectrum both before and after heating. After running the tube for four hours with as heavy a current as the tube would stand, without melting the electrode, the charcoal was cooled with liquid air; there was not a trace of any gas unabsorbed; hydrogen, helium, and neon were absent.

The charcoal was then heated in a sulphur bath; the discharge tube and the magnesium, etc., were also heated, and the xenon pumped out; 0·78 c.c. was obtained. The gas was put back into the apparatus, and again sparked for four hours. On pumping out as before only 0·60 c.c. of xenon was obtained. On repeating the experiment and again sparking after two and a half hours, the electrodes were sparking badly from the platinum wire fused into the aluminium, so the xenon was again pumped out; it had then become 0·50 c.c.

The tube as it was sparking so unsatisfactorily was sealed off, and another one made with electrodes of aluminium 4 mm. thick. After five hours sparking, again the discharge from the cathode was working badly, so the xenon was again pumped out; it had become 0·25 c.c. This tube was also sealed off, and a new one made with thick platinum electrodes. In this tube the xenon rapidly disappeared, and at the end of five hours sparking, with the cathode red hot, a phosphorescent vacuum remained, and the heated platinum splash refused to give up any gas.

It is unnecessary to give an account of all the experiments that were made, but the same disappearance of the xenon always took place. Hydrogen, helium, and neon were often tested for, but not a trace was ever noticed. Platinum seems to be the best metal to use, possibly because one can heat the cathode up to a bright red heat, and pass very heavy currents through the tube. Aluminium comes next, and copper next. With copper, although a very large amount of the cathode is volatilised, the disappearance of the xenon proceeds only slowly. Cadmium and zinc fuse too readily, and do not give good results, for, unless the cathode is heated almost red hot, very little xenon disappears.

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* 'Roy. Soc. Proc.,' A, vol. 90, p. 550 (1914).

To ascertain what had become of the xenon, the metallic splash was first examined; for, although xenon was not given off from it by heating, it might be liberated when the metal was dissolved. The first tube in which the 0·55 c.c. xenon had disappeared was therefore opened. The top containing the splash was at once broken up and put into an apparatus that could be evacuated by the pump. On to it was then run a solution of caustic soda, made from sodium, alcohol, and distilled water, and then boiled, to expel all the alcohol and dissolved gases. The gas that was evolved from the solution of the metal was put at once into the apparatus, by heating the magnesium, copper, and copper oxide, the hydrogen was converted into water that was absorbed by the phosphorus pentoxide, and there remained finally a trace of xenon, just sufficient to show the characteristic spectrum, but not enough to pump off from the apparatus. It was less than 0·05 c.c.

The aluminium electrode was next treated in the same way after about 500 c.c. of hydrogen had been evolved, the hydrogen was exploded with successive amounts of pure oxygen, and finally put into the apparatus, where the remainder of the hydrogen was got rid of. Not a trace of xenon could be detected, a phosphorescent vacuum remained, through which the spark would hardly pass. The glass of the tube was next treated with calcium fluoride and sulphuric acid, but no xenon could be found in the gas that was produced.

The caustic soda solution of the aluminium was neutralised and tested with silver nitrate; a faint precipitate was formed; it was not iodide of silver, probably it may have been silicate of silver. Barium chloride also gave no precipitate.

Xenon was also sparked for 12 hours with oxygen. After the oxygen had been removed by phosphorus, there was no diminution in the volume of the gas, and the spectrum was that of pure xenon.

Taking the results of all the experiments made, between 2 c.c. and 2·5 c.c. of xenon had disappeared. The gas has not been occluded either in the electrodes, or the metallic splash, or in the glass, for it ought to be set free again when they are dissolved. That it has formed some sort of compound is the most likely explanation, but, if so, why does it not appear again in the gases produced when the splash, etc., are dissolved? One would expect to find it as a hydride, but no such gas was found. That xenon may possibly form compounds has already been suggested by Dr. Whytlaw-Gray, Patterson, and Cripps, in a paper* on the critical constants of xenon.

They say, "we wish to draw attention to some curious effects noticed during the research." These curious effects were that, under certain conditions, the xenon, when compressed in an Andrews apparatus, did not behave as a pure liquid free from uncondensable gas. Moreover, when its density was determined, it came out too low. The xenon that behaved thus abnormally was obtained in different ways:—

(1) Xenon passed over copper oxide and lead chromate heated.

(2) Sparked with oxygen and then treated with solid potash, afterwards solidified by liquid air, and the oxygen pumped off. (Xenon, however, when mixed with pure oxygen and treated in a similar manner, gave pure xenon.)

(3) A mixture of oxygen and xenon was sparked at ordinary temperatures, also submitted to the silent electric discharge, also sparked at low temperatures. All these methods gave an impure xenon, but perfectly pure xenon could be obtained from these impure specimens by sparking them with pure hydrogen, freezing out the xenon by liquid air, and pumping off the hydrogen. The xenon then had the correct density, and in the Andrews apparatus behaved as a perfectly pure gas.

They made a large number of experiments to prove the existence of an oxide of xenon, but without results. But since xenon is monatomic, the density of any oxide must exceed that of the pure gas, the density, however, always came out too low. If, on the other hand, the impurity was oxygen, the amount, calculated from the density, corresponds to as much as 4–5 per cent. of free oxygen, and they were unable to detect any oxygen in the xenon. They conclude: "Although the experiments just described yielded no definite results, they show how oxygen can associate itself with xenon in such a way that the presence of the less condensable gas almost escapes detection."

The same may be said of these experiments with xenon in vacuum tubes: they have yielded no definite result. The spectrum in the tubes remained a perfectly pure spectrum from the beginning of the experiment to the end. If the xenon has formed some compound with metals of the electrodes, it certainly is not given off as a gas when the metallic compound is dissolved in sodium hydrate. Acids were also used for dissolving the metallic splash, with negative results.

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* 'Roy. Soc. Proc.,' A, vol. 86, p. 579 (1912).

If the xenon is present as a metallic compound, it must therefore go into solution as a compound on dissolution. Silicon hydrides, when treated with sodium hydrate, gives sodium silicate; it may be that xenon behaves in a similar manner, and that a xenate of sodium is formed.

The Supply of Energy from and to Atmospheric Eddies.

By Lewis F. Richardson.

(Communicated by Sir Napier Shaw, F.R.S. Received March 9, 1920.)

Introduction.

This paper extends Osborne Reynold's theory of the Criterion of Turbulence, to make it apply to the case in which work is done by the eddies, acting as thermodynamic engines in a gravitating atmosphere. For simplicity, the air is supposed to be dry. The gist of the solution is contained in equations (4·15) and (5·3) below.

Some analogies to thermodynamics are then introduced, including the conception of an eddy-heat-per-mass, and its diminution when the air expands. These conceptions are helpful in discussing the manner in which eddies diffuse. I am indebted to Mr. W. H. Dines, F.R.S., for his valuable advice at many stages of this work.

While it was being finished off, a treatment of the Criterion of Turbulence, by Wilhelm Schmidt, of Vienna,* has come to hand. For the supply of energy from the wind, he gives much fuller observational data than I have done. But, for the thermodynamic loss, he concludes that the activity per volume has the average value $b\partial^2\theta/\partial h^2$ where b is the gas constant in erg units, θ is the absolute temperature, and h the height. This is incompatible with the result arrived at in equation (4·15) below, and is, moreover, difficult to reconcile with observation. I am inclined to think that Prof. Schmidt has accidentally admitted a factor, $p^{0·29}$, in the diffusion equation. On integrating partially, and taking account of boundary conditions, this change would explain the discrepancy, if the turbulence were independent of height, as he assumes.

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* 'Ann. der Hydrog. u. Mar. Meteorol.,' November-December, 1918.

[*Added May* 25, 1920.—At the meeting at which this paper was discussed Mr. G. I. Taylor mentioned some studies of stability which formed part of his Adams Prize Essay in 1914. The oscillations of superposed laminæ of different density became unstable when a criterion was reached which resembled (5·4) below, except that the numerical coefficient contained a factor of 2 or of 4 depending on the number of the laminæ. By a rough energy-method he had arrived at a numerical coefficient agreeing with that of (5·4). It is to be hoped that these investigations will appear in print.]

I. *The Available Forms of Energy.*

Since energy is conserved, we might find the supply to eddies by counting up the losses from all the other forms.

In order to relieve ourselves of the trouble of considering effects at vertical walls, let us consider a large volume of atmosphere, say that standing on a land area measuring 10 km. × 10 km. or larger. Let this area be A cm.^2.

Let $\bar{p}_G$ be the mean pressure at the earth's surface. Then the mass standing upon A is $A\bar{p}_G/g = M$, say. Let dM be an element of this mass. The changes of the energy present in this mass may be classified as

(i) Change of intrinsic thermal energy ΔI,

$$\Delta I = \int \gamma_v \,.\, \Delta\theta \,.\, dM, \tag{1·1}$$

where γ_v is the thermal capacity per mass at constant volume, and θ is the temperature.

(ii) Change of gravitational energy $\Delta\Gamma$,

$$\Delta\Gamma = \Delta \int ghdM, \tag{1·2}$$

where h is the height of dM and g is the acceleration of gravity.

(iii) Imagine the wind velocity to be smoothed, so as to remove the gusts. Let v_X, v_Y, v_H be the actual winds; let $\bar{v}_X, \bar{v}_Y, \bar{v}_H$ be the means of the same. The means may be supposed to be taken over a time-interval, long compared with gusts, but short compared with the passage of barometric depressions.

Denote deviations from the mean by dashes, so that

$$v_X = \bar{v}_X + v_X'\,; \qquad v_Y = \bar{v}_Y + v_Y'\,; \qquad v_H = \bar{v}_H + v_H', \tag{1·3}$$

Square, add and multiply by half the density ρ, and again take the mean, denoted by a bar, over a similar interval of time. Then, as is well known, the terms containing products of means and deviations vanish, leaving

$$\tfrac{1}{2}\rho\,(v_X^2+v_Y^2+v_H^2) = \tfrac{1}{2}\rho\,(\bar{v}_X^2+\bar{v}_Y^2+\bar{v}_H^2)+\tfrac{1}{2}\rho\,(v_X'^2+v_Y'^2+v_H'^2), \tag{1·4}$$

so that the kinetic energy may be divided into that associated with the mean and that associated with the deviations. Denote these parts, for our large atmospheric block, by $\bar{E}$ and E' respectively, and their increases by $\Delta\bar{E}$ and $\Delta E'$. The object of this paper is to study $\Delta E'$.

By the continuity of energy

$$(\Delta I + \Delta\Gamma + \Delta\bar{E} + \Delta E')/\Delta t = G + R + W, \tag{1·5}$$

where G is the rate at which heat-energy is flowing into the large portion of atmosphere from the vegetation and ground or from the sea. And R is the excess of the radiation flowing in over that flowing out.

And W is the rate at which work is being transmitted across the vertical walls in the form of (pressure) × (velocity). As the size of the area A increases, W dwindles relatively to the other terms. Let us neglect W.

The immediate effect of the radiation R is to alter the temperature of the air, vegetation, land or sea. Afterwards, these temperature-changes may cause eddies. But in this paper we suppose that the temperature distribution is known. Therefore we may ignore radiation, provided that we also ignore the changes of temperature which it is at the instant producing. Let $\Delta_0 I$ be the change in the intrinsic energy *not* due to radiation. Accordingly (1·5), becomes

$$(\Delta_0 I + \Delta\Gamma + \Delta\bar{E} + \Delta E')/\Delta t = G. \tag{1·6}$$

This equation may be further simplified, for Mr. W. H. Dines has shown that there is a connection between the changes of gravitational and intrinsic energy.* On inserting the appropriate constants, γ_v the thermal capacity per mass at constant volume, and b the "gas constant" defined by the characteristic equation

$$p = b\rho\theta, \tag{1·7}$$

where ρ is density, Mr. Dines' theorem takes the following form: "*In a column of clear air bounded by vertical walls, and extending from the ground upwards to a height at which the pressure is negligible, the change in total gravitational energy, reckoned from the ground, is* b/γ_v *times the corresponding change in the total intrinsic energy.*" (1·8)

Now, $\gamma_v + b = \gamma_p$, where γ_p is the thermal capacity per mass at constant pressure. The theorem (1·8) may therefore be interpreted thus: a column of air, of unit mass, in cooling, gives out energy as if it had a specific heat γ_p. Of this energy, a part, b/γ_p, is due to the sinking of the column. (1·9)

So equation (1·6) simplifies to

$$\frac{\gamma_p}{\gamma_v}\frac{\partial_0 I}{\partial t} + \frac{\partial\bar{E}}{\partial t} + \frac{\partial E'}{\partial t} = G. \tag{1·10}$$

The whole energy is sometimes correctly classified in ways involving the pressure p. Margules,[*] for instance, calculates the energy associated with local irregularities of pressure. In the present scheme this energy comes in (i) and (ii), and, to include pressural energy in addition, would be to count some of the energy twice over. It seems to be most natural to regard pressure only as concerned in the transfer across surfaces. Once across, energy appears in some other form—gravitational, intrinsic, or molar kinetic.

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* 'Q. J. Roy. Met. Soc.,' p. 188, July, 1913.

II. *The Supply from the Mean Wind.*

Osborne Reynolds[†] showed that the kinetic energy of eddying was increased by the work done by the eddy-stresses upon the corresponding rates of mean strain.

In the atmosphere, high above trees and houses, many of the rates of mean strain are negligible, and the activity may be abbreviated to

$$\text{activity per volume} = \widehat{xh}\,\frac{\partial \bar{v}_{\mathrm{X}}}{\partial h} + \widehat{yh}\,\frac{\partial \bar{v}_{\mathrm{Y}}}{\partial h}, \tag{2·1}$$

where $\widehat{xh}$, $\widehat{yh}$, are the shearing stress on horizontal planes and where h is the upward co-ordinate.

If μ be the "eddy viscosity" defined as

$$\mu = \frac{\text{eddy shearing stress}}{\text{corresponding rate of mean shear}}. \tag{2·2}$$

Then equation (2·1) may be written

$$\text{activity per volume} = \mu_{\mathrm{XH}}\left(\frac{\partial \bar{v}_{\mathrm{X}}}{\partial h}\right)^2 + \mu_{\mathrm{YH}}\left(\frac{\partial \bar{v}_{\mathrm{Y}}}{\partial h}\right)^2, \tag{2·3}$$

where μ_{XH} and μ_{YH} are possibly not equal, as suggested by the author,[‡] expressing the rate at which the mean-wind gives up its energy to eddies. Numerical data, based on observation, are collected by H. U. Sverdrup.[§]

III. *The Loss by Molecular Viscosity.*

Reynolds[||] balances the above gain of energy against the energy converted into heat at a rate per volume equal to

$$\mu_c\left\{2\left(\frac{\partial v_{\mathrm{X}}'}{\partial x}\right)^2 + 2\left(\frac{\partial v_{\mathrm{Y}}'}{\partial y}\right)^2 + 2\left(\frac{\partial v_{\mathrm{H}}'}{\partial h}\right)^2 + \left(\frac{\partial v_{\mathrm{H}}'}{\partial y} + \frac{\partial v_{\mathrm{Y}}'}{\partial h}\right)^2 + \left(\frac{\partial v_{\mathrm{X}}'}{\partial h} + \frac{\partial v_{\mathrm{H}}'}{\partial x}\right)^2 + \left(\frac{\partial v_{\mathrm{Y}}'}{\partial x} + \frac{\partial v_{\mathrm{X}}'}{\partial y}\right)^2\right\}, \tag{3·1}$$

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[*] "The Mechanical Equivalent of Pressure," 'Abbe's Translations,' 3rd series, Smithsonian Publications.

[†] Lamb, 'Hydrodynamics,' 4th ed., §369.

[‡] 'Phil. Trans.,' A, p. 1 (1920).

[§] 'Geo. Inst., Leipzig,' 2nd ser., Band II, Heft 4.

[||] Lamb, 'Hydrodynamics,' 4th ed., p. 369.

where μ_c is the molecular viscosity and dashes denote deviations from the mean.

This rate of loss will vanish if the eddying energy vanishes, for then v_X', v_Y', v_H' will be zero everywhere. Further, it is clear that the loss by molecular viscosity increases with the eddying velocities and with the smallness of the eddies.

The expression (3·1) when integrated over the volume standing on the large area A will be denoted by $-\left(\frac{\partial E'}{\partial t}\right)_1$.

The suffix is necessary because it is not the only part of $\frac{\partial E'}{\partial t}$.

To gain some rough idea of the numerical value of the dissipation, let us imagine that the complicated irregular motion is analysed into a series of regular motions superposed upon one another according to the method of Fourier. In other words, let each component of the instantaneous velocity be expanded in sines and cosines of each of the co-ordinates. Let us pick out for examination the terms

$$\left.\begin{aligned} v_X' &= B \sin\frac{\pi x}{n_X}\cos\frac{\pi y}{n_Y}\sin\frac{\pi h}{n_H} \\ & \qquad\qquad\qquad\qquad\qquad ;\ v_Y' = 0 \\ v_H' &= B\cos\frac{\pi x}{n_X}\cos\frac{\pi y}{n_Y}\cos\frac{\pi h}{n_H} \end{aligned}\right\} \tag{3·2}$$

which signifies a motion divided up into rectangular cells, so that the eddies would look rather like papers curled up in the pigeonholes of an office desk. The size of the cell is n_X by n_H centimetres in the plane of the motion, and n_Y at right angles to the motion.

The mean kinetic energy associated with this distribution is got by squaring the trigonometrical terms and integrating over a volume of atmosphere very large compared with the size of the cell. Taking the mean with respect to any one co-ordinate replaces the square of a sine or cosine by $\frac{1}{2}$. So the three successive operations introduce the factor $(\frac{1}{2})^3$, and the mean kinetic energy is therefore

$$\tfrac{1}{2}\rho\left(v_X'^2+v_Y'^2+v_H'^2\right) = \tfrac{1}{2}\rho\left\{\tfrac{1}{8}+0+\tfrac{1}{8}\right\} = \tfrac{1}{8}\rho B^2 = E'/(\text{the large volume}). \tag{3·3}$$

Next to find the rate of dissipation we have to insert v_X', v_Y', v_H' in the dissipation function quoted above. The differentiations introduce factors π/n_X, π/n_Y, π/n_H. The term $\partial v_X/\partial h+\partial v_H/\partial x$ conveniently vanishes. Squaring and taking the mean over a large volume again introduces the factor $\frac{1}{8}$. So that the mean rate of dissipation comes to

$$2\mu_c\pi^2\left\{\frac{1}{n_X{}^2}+\frac{1}{n_Y{}^2}+\frac{1}{n_H{}^2}\right\}\tfrac{1}{8}B^2 = \frac{\partial E'}{\partial t}\,\frac{1}{(\text{the large volume})}. \tag{3·4}$$

The quantity $(n_X^{-2}+n_Y^{-2}+n_H^{-2})$ is a measure of the smallness of the eddy. Let us denote it by l^{-2}, so that we may speak of l as the linear size of an eddy. If the cell which encloses the eddy were cubical, then l would be 0·577 of the edge of the cube. If the cube were drawn out into a very long square prism, then l would be 0·707 of the side of the square. If the prism were stretched into a plate, l would be the thickness of the plate.

Then from (3·3) and (3·4)

$$\frac{\partial E'}{\partial t} = \frac{2\mu_c \pi^2}{\rho l^2} E'. \tag{3·5}$$

Now $\mu_c = 1{\cdot}7 \times 10^{-4}$ for air at 273° A.

So if l be say 10 metres

$$\frac{1}{E'}\frac{\partial E'}{\partial t} = 2{\cdot}6 \times 10^{-6}\,\text{sec}^{-1}.$$

So that after 24 hours the eddying energy would have fallen to 0·8 of its initial value. The changes which we observe near the ground are much more rapid, so that either the eddies must be smaller than the size represented by $l = 10$ metres, or else other causes than molecular viscosity must cooperate to destroy the eddying energy.

We will not now stop to inquire what would be the interaction on the average between eddies of different sizes and positions represented by the different terms of the Fourier expansion. The equation (3·5) is to be understood as a type, not as a complete formulation.

IV. *Convection.*

The rising of cumuli during the daytime and the diminution of turbulence in the surface wind on clear nights both shows us that convection has an important influence.

The eddies are themselves the engines by which the available heat is converted into their visible motion, so that the rate of conversion must depend somehow upon the rate of eddying. Let us explore this question.

But the eddies are imperfect engines, for they lead to mixing of portions of air at different temperatures, and mixing is an irreversible process. If, however, we can by any means find the diminution of the intrinsic heat energy of the atmosphere, we shall be able to find the energy supplied to the eddies, at least if the air be dry, by the aid of the theorem of Section 1 given by Mr. W. H. Dines.*

Now we can find the rate of change of intrinsic energy in terms of the rate of eddying, by means of the equation for the diffusion of potential temperature, denoted by Φ,

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* 'Q. J. Roy. Met. Soc.,' p. 188, July, 1913.

$$\frac{\bar{D}\Phi}{\bar{D}t} = \frac{\partial}{\partial p}\left(\xi \frac{\partial \Phi}{\partial p}\right), \tag{4·1}$$

where p is pressure used as a measure of depth, and where ξ is a measure of turbulence, for which I have suggested the name "turbulivity." In quoting this equation from a previous paper it is necessary to make clear three points which I then* left confused. For we are now examining small effects, and precision in details is essential to success.

(i) When there are no eddies we are accustomed to compute the flow of heat or of water vapour across a plane from the flow of mass across the plane. As the effect of eddies is to be treated as additional, we should not include in it any flow due to the mean motion of mass across a plane, and accordingly $\bar{D}$ is here a differentiator which follows the *mean* motion of the fluid, in the sense that the effect of eddies is to cause equal masses to cross the co-ordinate surface from opposite sides. In the case in which there is no convergence of air in the general circulation, $\bar{D}$ accordingly refers to a surface of fixed pressure, not to one of fixed height. Therefore, as p is the other independent, $\bar{D}/\bar{D}t$ may be replaced by curly $\partial/\partial t$, indicating differentiation at constant pressure.

(ii) Secondly, the equation would not hold if entropy per mass, σ, were substituted in place of Φ, because entropy is increased by mixing. In fact, as for dry air,

$$d\sigma = \gamma_p d \log \Phi \tag{4·2}$$

the equation for the diffusion of σ takes the different form

$$\frac{\partial e^{\sigma/\gamma_p}}{\partial t} = \frac{\partial}{\partial p}\left(\xi \frac{\partial e^{\sigma/\gamma_p}}{\partial p}\right). \tag{4·3}$$

(iii) The eddy motion produces an atmosphere with an intricate structure; but as the diversity is smoothed out by molecular diffusion at constant pressure, the mean value of Φ for a secluded portion of air remains unchanged. Therefore in equation (4·1) we may regard Φ as a mean value over a portion of an isobaric surface.

With this explanation let us return to (4·1), and deduce from it the rate of change of temperature.

For dry air

$$\Phi = \theta\left(\frac{p_i}{p}\right)^{0·29} \tag{4·4}$$

where p_i is the standard pressure adopted in defining Φ.

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* 'Roy. Soc. Proc.,' A, London, vol. 96, p. 10 (1919).

So, at constant pressure

$$\frac{\partial \Phi}{\partial t} = \left(\frac{p_i}{p}\right)^{0\cdot 29} \cdot \frac{\partial \theta}{\partial t}. \tag{4·5}$$

Insert this in (4·1), transfer the factor in $p^{0\cdot 29}$ to the other side of the equation, multiply by γ_p and integrate from the top to the bottom of the atmosphere, with respect to the element of mass per unit horizontal area dp/g

$$\frac{\gamma_p}{g}\int_0^G \frac{\partial \theta}{\partial t}\,dp = \frac{1}{p_i^{0\cdot 29}}\,\frac{\gamma_p}{g}\int_0^G p^{0\cdot 29}\,\frac{\partial}{\partial p}\left(\xi\,\frac{\partial \Phi}{\partial p}\right)dp. \tag{4·6}$$

Integrate the second member by parts

$$\frac{\gamma_p}{g}\int_0^G \frac{\partial \theta}{\partial t}\,dp = \gamma_p\,{}_0^G\!\left[\frac{\theta}{\Phi}\,\frac{\xi}{g}\,\frac{\partial \Phi}{\partial p}\right] - \frac{1}{p_i^{0\cdot 29}}\,\frac{\gamma_p}{g}\int_0^G \xi\,\frac{\partial \Phi}{\partial p}\,d\left(p^{0\cdot 29}\right) \tag{4·7}$$

The two terms on the right are both activities due to convection per unit horizontal area. They may be distinguished as the "boundary activity" and the "body activity" respectively. The boundary activity must vanish at the top of the atmosphere. The sign of the second integral in (4·7) determines whether, in the body of the atmosphere, heat is being transformed to eddying energy or *vice versâ*.

Now ξ is essentially positive and so is $d(p^{0\cdot 29})$, since the integration is made downwards. Therefore (4·7) implies that heat becomes eddying energy if the potential temperature increases downwards. That is what we should expect. If there were no eddying, ξ would vanish and equation (4·7) would correctly indicate no activity. The atmosphere might then be unstable, but if so, it would be at rest in equilibrium—a hypothetical case merely.

Consider the boundary activity in equation (4·7). Now, in the paper* referred to it is shown that $\xi/g\,.\,\partial\Phi/\partial p$ is the amount of Z rising across surface per area per time, when Z is defined by the statement that Φ is the amount of Z per unit mass of atmosphere, and the surface ought to have been specified as one crossed by equal masses from opposite sides. Thus equation (4·7) shows that the boundary convective activity is simply the rate at which eddies remove heat energy from the ground, vegetation, or sea per horizontal square centimetre.

To correspond with the equation of continuity of energy in the form (1·10) of Section I, we must integrate (4·7) over the large horizontal area A. When so integrated, the boundary activity per area becomes what we have formerly denoted by G. And the first member is γ_p/γ_v times the whole rate of increase in intrinsic energy, not arising from radiation, nor from dissipation of eddying kinetic energy by molecular viscosity. So we obtain for the integral of the body activity, the following expression:—

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* 'Roy. Soc. Proc.,' A, London, vol. 96, p. 11 (1919) equation (16).

$$\frac{\gamma_p}{\gamma_v}\frac{\partial_0 \mathrm{I}}{\partial t} - \mathrm{G} = -\iint\left[p_i^{-0\cdot 29}\frac{\gamma_p}{g}\int_0^{\mathrm{G}}\xi\frac{\partial\Phi}{\partial p}\,dp^{0\cdot 29}\right]d\mathrm{A}. \tag{4·8}$$

This expression can be much simplified by using the following relations

$$\xi = g^2\rho c, \text{ where } c \text{ is eddy conductivity} \tag{4·9}$$

$$p = b\rho\theta \text{ (gas equation)}, \tag{4·10}$$

$$\frac{\partial p}{\partial h} = -g\rho \text{ (hydrostatic equation)}, \tag{4·11}$$

$$d\sigma = \gamma_p d\log\Phi = \gamma_p d\log\theta - bd\log p, \tag{4·12}$$

$$\left(\frac{p_i}{p}\right)^{0\cdot 29} = \frac{\theta}{\Phi} \text{ (definition of potential temp.)}. \tag{4·13}$$

The stages by which the transformation takes place may be as follows:—

$$-\frac{1}{p_i^{0\cdot 29}}\frac{\gamma_p}{g}\int_0^{\mathrm{G}}\xi\frac{\partial\Phi}{\partial p}\,dp^{0\cdot 29} = -\frac{\gamma_p}{g}\int_0^{\mathrm{G}}g^2\rho c\frac{\partial\Phi}{\partial p}d\left(\frac{\theta}{\Phi}\right) = \gamma_p\int_0^{\mathrm{G}}c\frac{\partial\Phi}{\partial h}\left\{\frac{d\theta}{\Phi}-\frac{\theta}{\Phi^2}d\Phi\right\}$$

$$= \int_0^{\mathrm{G}}c\frac{\partial\sigma}{\partial h}\left\{d\theta-\theta d\log\Phi\right\} = \int_0^{\mathrm{G}}c\frac{\partial\sigma}{\partial h}\frac{b\theta}{\gamma_p}\frac{dp}{p} = -\frac{g}{\gamma_p}\int_0^{\mathrm{G}}c\frac{\partial\sigma}{\partial h}\,dh. \tag{4·14}$$

The last form is the simplest. When inserted in (4·8) the latter becomes

$$\frac{\gamma_p}{\gamma_v}\frac{\partial_0 \mathrm{I}}{\partial t} - \mathrm{G} = +\iint\left[\frac{g}{\gamma_p}\int_{\mathrm{G}}^{0}c\frac{\partial\sigma}{\partial h}\,dh\right]d\mathrm{A}. \tag{4·15}$$

In words this may be stated as follows:—*The average rate at which intrinsic and gravitional energy jointly are being transformed into the energy of eddies is equal per volume to* $\partial\sigma/\partial h \times cg/\gamma_p$, *that is to say to the product of the eddy conductivity into the acceleration of gravity into the gradient of entropy per mass upward, divided by the thermal capacity per mass at constant pressure.*

Now there exist observations of c and of $\partial\sigma/\partial h$. So let us divide the activity per volume $cg/\gamma_p \times \partial\sigma/\partial h$ into the factors c and $g/\gamma_p \times \partial\sigma/\partial h$ and make a table of the latter under average conditions. For computing $\partial\sigma/\partial h$ from observations, a convenient formula is

$$\frac{\partial\sigma}{\partial h} = \frac{1}{\theta}\left\{\gamma_p\frac{\partial\theta}{\partial h}+g\right\}, \tag{4·16}$$

it applies accurately to dry air, and with quite small errors to clear moist air when γ_p has its value for dry air. So I have taken data for clear days where such data were available. It is not worth considering cloudy days until the theory can be arranged *throughout* for that purpose, and that would very greatly add to its complexity.

Table I.

(Computed from Josef Reger's Analysis of the Lindenberg Observations,* clear days only.)

Hour (0 = midnight).	2.	8.	14.	20.
Layer, metres above M.S.L.	$g/\gamma_p\, \partial\sigma/\partial h$ expressed in sec.$^{-2}$ equals $10^{-4}\times$ the following			
122 to 500	6·52	3·02	−0·31	2·54
500 1000	1·50	1·95	0·76	1·07
1000 1500	1·83	1·70	1·46	0·88
1500 2000	2·51	1·20	1·47	0·20

Table II.[†]

(England, S.E., days both clear and cloudy.)

Height.	$g/\gamma_p\, \partial\sigma/\partial h$ in sec.$^{-2}$	Height.	$g/\gamma p\, \partial\sigma/\partial h$ in sec.$^{-2}$.	
km.	$10^{-4}\times$	km.	$10^{-4}\times$	
13·5	4·42	6·5	1·07	
12·5	4·74	5·5	1·20	
11·5	4·07	4·5	1·28	‡
10·5	3·03	3·5	1·47	
9·5	2·59	2·5	1·66	
8·5	1·49	1·5	1·92	
7·5	1·01			

‡ Doubtful, owing to formula for dry air having been used.

These Tables show that on clear days in the troposphere $g/\gamma_p . \partial\sigma/\partial h$ is of the order of 10^{-4} sec.$^{-2}$ on the average.

Now the eddy conductivity at the height of a kilometre has been found by numerous observers to be of the order of 100 grm. sec.$^{-1}$ cm.$^{-1}$.

Taking these numbers it follows that $cg/\gamma_p . \partial\sigma/\partial h = 10^{-2}$ erg. sec.$^{-1}$ cm^{-3}. This is the convective activity per volume lost by the eddies.

V. *Joint Effects of the Various Supplies.*

In the equation of continuity in the form (1·10) let us now insert the convective activity given by (4·15) together with Reynold's expression for the supply of energy from the mean wind (2·3). The result is

$$\frac{\partial \mathrm{E}'}{\partial t} = \iint \left\{ \mu \left(\frac{\partial \bar{v}_{\mathrm{X}}}{\partial h} \right)^2 + \mu \left(\frac{\partial \bar{v}_{\mathrm{Y}}}{\partial h} \right)^2 \right\} dh\, d\mathrm{A} - \int \left[\frac{g}{\gamma_p} \int_{\mathrm{G}}^{0} c \frac{\partial \sigma}{\partial h}\, dh \right] d\mathrm{A}. \qquad (5·1)$$

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* Vieweg und Sohn, Braunschweig, 'Arbeiten des K. P. Aeronautischen Observatoriums bei Lindenberg,' vol. 8, p. 247 (1912).

[†] Computed from 'Characteristics of the Free Atmosphere,' by W. H. Dines, p. 62.

In reckoning the change of temperature due to convection, we took no account of the heat produced by the dissipation of eddy motion by molecular viscosity. So that $\partial E'/\partial t$, as just given, ought to be decreased by the quantity (3·5) and a completer formulation is therefore :—

$$\frac{\partial E'}{\partial t} - \frac{2\mu_c\pi^2}{\rho l^2}E' = \iint\left\{\mu\left(\frac{\partial \bar{v}_X}{\partial h}\right)^2 + \mu\left(\frac{\partial \bar{v}_Y}{\partial h}\right)^2\right\} dh\, dA - \int\left[\frac{g}{\gamma_p}\int_G^0 c\frac{\partial\sigma}{\partial h}dh\right]dA. \tag{5·2}$$

Now G. I. Taylor* put forward the hypothesis that the eddy viscosity $\mu =$ eddy conductivity c, and observation has so far tended to confirm this. Let us make this simplification. Then (5·2) becomes

$$\frac{\partial E'}{\partial t} - \frac{2\mu_c\pi^2}{\rho l^2}E' = \iint c\left\{\left(\frac{\partial \bar{v}_X}{\partial h}\right)^2 + \left(\frac{\partial \bar{v}_Y}{dh}\right)^2 - \frac{g}{\gamma_p}\frac{\partial\sigma}{\partial h}\right\} dh\, dA. \tag{5·3}$$

This is a very interesting equation. To take a special application of it, suppose that the large piece of atmosphere, throughout which the integral is taken, is initially at rest. Suppose next that an approaching depression sets it in motion. Will the winds be turbulent or not? Suppose that they are very slightly turbulent, so that c and E' are just not zero, but so that $2\mu_c\pi^2E'/(\rho l^2)$ is very small. The question is: will E' increase? It will tend to increase if

$$\left(\frac{\partial \bar{v}_X}{\partial h}\right)^2 + \left(\frac{\partial \bar{v}_Y}{\partial h}\right)^2 > \frac{g}{\gamma_p}\frac{\partial\sigma}{\partial h}. \tag{5·4}$$

If the atmosphere has the ordinary value of $g/\gamma_p \cdot \partial\sigma/\partial h$ equal to say $+10^{-4}$ sec.$^{-2}$, then the wind will become turbulent if the change of velocity with height exceeds $\pm\sqrt{10^{-4}\,\text{sec.}^{-2}}$. That is to say, a change of about 1 metre sec.$^{-1}$ in 100 metres of height would be the critical value on an average clear day in the troposphere. Now pilot balloon ascents† show such up-grades generally in the first 100 metres above ground and frequently up to a kilometre. But above a kilometre such up-grades are rather uncommon until the base of the stratosphere is reached, where again there is a rapid change.‡ But at this height, as Table II shows, $g/\gamma_p \cdot \partial\sigma/\partial h$ has increased considerably, so that a more rapid variation of wind, say 18 metres sec.$^{-1}$ per kilometre of height, would be required to produce turbulence. The stability of the stratosphere is well shown by the large value of $g/\gamma_p \cdot \partial\sigma/\partial h$. We conclude then that the usual source of atmospheric eddies is in the first few hundred metres, and that they may sometimes be formed at the base of the stratosphere.

The limit to E' will be set by the dissipation term $2\mu_c\pi^2E'/\rho l^2$.

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* 'Phil. Trans.,' A, 1914.

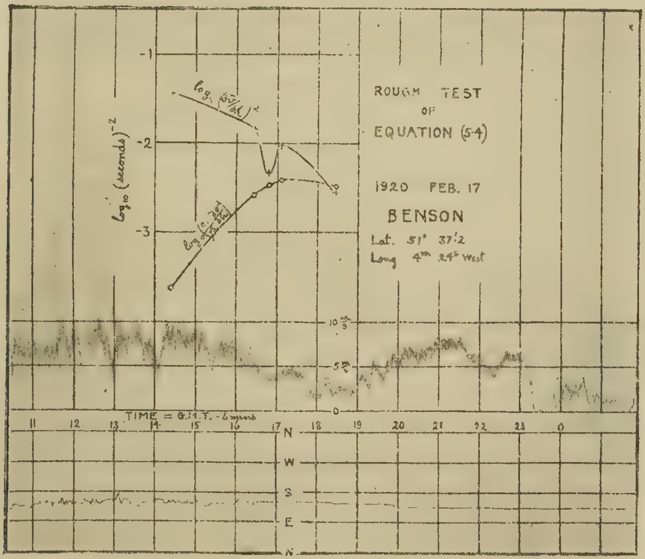
† 'Manual of Meteorology,' by Sir Napier Shaw, Part IV, Ch. VI.

‡ G. M. B. Dobson, 'Q. J. Met. Soc.,' Jan., 1920.

Stirring a dry atmosphere tends to bring the entropy-gradient, $\partial\sigma/\partial h$, towards zero. So if the atmosphere is originally stable, equation (5·3) indicates that the more it is stirred the easier does it become to stir.

The dying away of the surface wind at night has for some time been explained as an effect of radiation, which by increasing $\partial\sigma/\partial h$ makes the lower layers too stable for eddies to exist in them. Equation (5·3) conforms to this explanation and gives to it an expression which is quantitative. Equation (5·3) also shows that, when the day wind is sufficiently strong $(\partial\bar{v}/\partial h)^2$ will overpower the term in $\partial\sigma/\partial h$, so that eddies will continue to exist and to supply momentum to the surface air, even on a clear night. That fits with observation. At Benson, for example, where the anemometer head is 26 metres above the plain, the day wind usually dies away on a clear winter night if it is 5 metres/sec. but not if it is 11 metres/sec., provided that evenings on which the barometric gradient is changing rapidly are excluded.

A theory like this one, which supposes the mean velocities to be in horizontal straight lines, can only fit with observation at a height above the ground which is large compared with the irregularities of the surface.



To make a proper test of equation (5·4) the following installation would be suitable: Two anemometers, one above the other, to determine $\partial\bar{v}/\partial h$; the lower should be at a height large compared with the local irregularities on the ground; a differential thermometer to read the difference of temperature between these two anemometer heads; and a pressure tube anemometer placed at an intermediate level to record the range of the gusts. I am not aware of the existence of such an installation.

Choosing an occasion at Benson, when trees interfered as little as possible with the wind currents, I obtained the results shown in the figure. The temperature readings were taken with an aspirated thermometer. *It is seen that the approach of the curves* for $\log_{10}\left(\frac{g}{\gamma_p}\frac{\partial\sigma}{\partial h}\right)$ and $\log_{10}\left(\frac{\partial v}{\partial h}\right)^2$ *coincides in time at* 16 h. 40 m. *with a marked decrease in the range of the gusts shown by the anemometer.* A perfect agreement could not be expected because $\partial v/\partial h$ was measured over the interval 1 m. to 26 m., while $\partial\sigma/\partial h$ only over the interval 1 m. to 16 m. Again it would have been better if gustiness could have been measured at the average height, but trees prevented this. On this night the wind did not die away after sunset, but the current from 19 h. to 23 h. is probably the katabatic wind from the Chiltern Hills described by Mr. E. V. Newham in M. O. Professional Notes No. 2.

VI. *The Irreversibility of Convection.*

We may think of this by the aid of the resulting increase of the total entropy S in an atmospheric column standing upon a horizontal unit area. Since $\partial p/g$ is the mass in the short length of the column

$$\frac{d\mathrm{S}}{dt} = \frac{1}{g}\int_0^{\mathrm{G}} \frac{\partial\sigma}{\partial t}\,dp. \tag{6·1}$$

But (4·1) with (4·2) gives as an alternative form of (4·3)

$$\frac{\partial\sigma}{\partial t} = \frac{1}{\Phi}\left(\xi\Phi\frac{\partial\sigma}{\partial p}\right). \tag{6·2}$$

Inserting this in (6·1) and integrating by parts

$$\frac{d\mathrm{S}}{dt} = \frac{1}{g}\int_0^{\mathrm{G}}\frac{1}{\Phi}\frac{\partial}{\partial p}\left(\xi\,\Phi\frac{\partial\sigma}{\partial p}\right)dp = {}_0^{\mathrm{G}}\left[\frac{\xi}{g}\frac{\partial\sigma}{\partial p}\right] + \frac{1}{g}\int_0^{\mathrm{G}}\xi\,\Phi\frac{\partial\sigma}{\partial p}\,\frac{\partial\Phi}{\Phi^2\partial p}\,dp. \tag{6·3}$$

The integrated term is simply the rate at which entropy is entering the column from the earth's surface. Remembering that $d\sigma = \gamma_p.d\log\Phi$ the remaining integral may be written in alternative forms as follows :—

$$\frac{d\mathrm{S}}{dt} - \left[\frac{\xi}{g}\frac{\partial\sigma}{\partial p}\right]_{\mathrm{G}} = \frac{1}{g\gamma_p}\int_0^{\mathrm{G}}\xi\left(\frac{\partial\sigma}{\partial p}\right)dp = \gamma_p\int_{\mathrm{G}}^0 c\left(\frac{\partial\log\Phi}{\partial h}\right)^2 dh = \frac{1}{\gamma_p}\int_{\mathrm{G}}^0 c\left(\frac{\partial\sigma}{\partial h}\right)^2 dh. \tag{6·4}$$

This quantity is essentially positive as we should expect, since the entropy cannot decrease. It shows that the rate of increase of entropy depends upon the square of $\partial\sigma/\partial h$, whereas the rate at which eddying energy is converted into heat depends upon the first power of the same, see (4·15). Thus the nearer the gradient of entropy approaches to zero the more nearly will the eddies approach to perfectly reversible engines. If the eddy conductivity c were confined to a range of height in which $\partial\sigma/\partial h$ were constant, so that we might remove the integral signs, then dividing the last form of (6·4) by the last of (4·14) it would follow that

$$\frac{\text{increase of entropy}}{\text{energy supplied from eddies}} = \frac{1}{g}\frac{\partial\sigma}{\partial h}. \tag{6·5}$$

Multiplying by the temperature θ of the layer we should find

$$\frac{\text{energy made unavailable}}{\text{energy supplied from eddies}} = \frac{\theta}{g}\frac{\partial\sigma}{\partial h}. \tag{6·6}$$

This fraction is a pure number, which has an average value of about one-third in the troposphere. We see from (4·16) that in an isothermal atmosphere it would have the value unity. In an adiabatic atmosphere it is zero.

VII. *Eddy Thermodynamics.* (Revised May 11, 1920.)

The direct eddy stresses are, according to O. Reynolds

$$\overset{\frown}{xx} = -\rho\overline{v_{\text{X}}{}'v_{\text{X}}{}'}; \qquad \overset{\frown}{yy} = -\rho\overline{v_{\text{Y}}{}'v_{\text{Y}}{}'}; \qquad \overset{\frown}{hh} = -\rho\overline{v_{\text{H}}{}'v_{\text{H}}{}'}, \tag{7·1}$$

when tractions are reckoned positive, and bars denote mean values, and dashes denote deviations from the mean.

Following custom in the theory of viscous fluids, we could define an "eddy pressure," $\wp$, as the negative mean of the direct tractions

$$\wp = -\tfrac{1}{3}(\overset{\frown}{xx}+\overset{\frown}{yy}+\overset{\frown}{hh}). \tag{7·2}$$

From (7·1) and (7·2) it follows that

$$\frac{\wp}{\rho} = \tfrac{2}{3}\cdot\overline{\tfrac{1}{2}(v_{\text{X}}{}'^2+v_{\text{Y}}{}'^2+v_{\text{H}}{}'^2)}. \tag{7·3}$$

This resembles the "gas equation" $\frac{p}{\rho} = b\theta$ and suggests that we might tentatively introduce the idea of "eddy-heat per mass," defined thus

$$\text{“eddy-heat per mass”} = \overline{\tfrac{1}{2}(v_{\text{X}}{}'^2+v_{\text{Y}}{}'^2+v_{\text{H}}{}'^2)} = \Theta \text{ say,} \tag{7·4}$$

so that

$$\wp = \tfrac{2}{3}\rho\Theta. \tag{7·5}$$

Next taking a suggestion from the adiabatic cooling of gases, *let us enquire whether the eddy-heat-per-mass would diminish if the air containing the eddies were suddenly expanded.* In this connection we must note that the energy per mass Θ, with which we are concerned, is not acoustical, and so moves with, not through, the fluid (Helmholtz, Kelvin). It is true that Θ as defined by (7·4) would include some acoustical energy, but let us suppose that sufficient time has elapsed to allow this to disperse itself with the speed of sound.

To obtain some light on the question, let us imagine a region containing a lively eddy motion accompanied by a mean-expansion. Reynolds' investigation relates to an incompressible fluid, so we must make a fresh start.

Consider a plane moving so that on the average as much mass crosses it from one side as from the other. For simplicity let the plane be set at right angles to $\bar{v}_X$. The molar kinetic energy in the fluid at any point is $\frac{1}{2}\rho(v_X{}^2+v_Y{}^2+v_H{}^2)$ per volume. And not being acoustical, it is moving with the velocity of the fluid v_X. As the plane is moving at the speed $\bar{v}_X$, the volume of fluid crossing an area dA of the plane in unit time is $(v_X-\bar{v}_X)\,dA$. So the mean rate at which molar kinetic energy crosses the plane is

$$\frac{1}{A}\int\tfrac{1}{2}\rho\,(v_X{}^2+v_Y{}^2+v_H{}^2)(v_X-\bar{v}_X)\,dA. \tag{7·6}$$

Now introduce dashes for variations from the mean so that

$$v_X=\bar{v}_X+v_X{}'\,;\qquad \rho=\bar{\rho}+\rho'\,;\qquad \text{and the like.} \tag{7·7}$$

Then (7·6) becomes, on squaring out,

$$\frac{1}{A}\int\tfrac{1}{2}(\bar{\rho}+\rho')\,\{\bar{v}_X{}^2+\bar{v}_Y{}^2+\bar{v}_H{}^2+2\bar{v}_X v_X{}'+2\bar{v}_Y v_Y{}'+2\bar{v}_H v_H{}' +v_X{}'^2+v_Y{}'^2+v_H{}'^2\}v_X{}'\,dA. \tag{7·8}$$

Now the mean values of the rapidly varying quantities, which are indicated by dashes, will approximately vanish when taken over a sufficiently large area. So also will vanish the mean of any dashed into any barred quantity, since the barred quantities vary slowly from point to point. Thus we may pick out from (7·8) the following terms which vanish:—

$$\frac{1}{A}\int\tfrac{1}{2}\bar{\rho}\,\{\bar{v}_X{}^2+\bar{v}_Y{}^2+\bar{v}_H{}^2\}v_X{}'\,dA=0. \tag{7·9}$$

Again, since an increase of density is as likely to be accompanied by a positive as by a negative $v_X{}'$, so the following terms in $\rho'v_X{}'$ vanish:—

$$\frac{1}{A}\int\tfrac{1}{2}\rho'\,\{\bar{v}_X{}^2+\bar{v}_Y{}^2+\bar{v}_H{}^2\}v_X{}'\,dA=0, \tag{7·10}$$

which is equivalent to assuming the absence of convection of mass.

In order to divide our difficulties, let us at this stage assume that

$$\frac{1}{A}\int\tfrac{1}{2}\rho\,(v_X{}'^2+v_Y{}'^2+v_H{}'^2)\,v_X{}'\,dA=0. \tag{7·11}$$

This assumption implies that the eddying kinetic energy per volume is not correllated with $v_X{}'$, so that portions of high energy are not moving specially to either side of the plane. That is to say, we have assumed no diffusion of eddying energy, from where it is intense to where it is feeble. We shall return to the question of diffusion in the next section.

Let (7·9), (7·10), (7·11) be assumed, then (7·8) simplifies to

$$\frac{1}{\mathrm{A}}\int(\bar{v}_{\mathrm{X}}\,\rho v_{\mathrm{X}}{}'v_{\mathrm{X}}{}' + \bar{v}_{\mathrm{Y}}\,\rho v_{\mathrm{Y}}{}'v_{\mathrm{X}}{}' + \bar{v}_{\mathrm{H}}\,\rho v_{\mathrm{H}}{}'v_{\mathrm{X}}{}')\,d\mathrm{A}. \tag{7·12}$$

Now, in conformity with Reynolds' statement of the eddy stresses, when the bar replaces $\frac{1}{\mathrm{A}}\int(\quad)\,d\mathrm{A}$ as an averaging operator, put to complete (7·1).

$$\overset{\frown}{xy} = -\overline{\rho v_{\mathrm{X}}{}'v_{\mathrm{Y}}{}'}\,; \qquad \overset{\frown}{yh} = -\overline{\rho v_{\mathrm{Y}}{}'v_{\mathrm{H}}{}'}\,; \qquad \overset{\frown}{hx} = -\overline{\rho v_{\mathrm{H}}{}'v_{\mathrm{X}}{}'}. \tag{7·13}$$

Then the mean rate at which molar kinetic energy is crossing unit area of a plane set at right angles to $\bar{v}_{\mathrm{X}}$ and moving with the fluid at its centre, becomes from (7·12)

$$-\bar{v}_{\mathrm{X}}\,.\,\overset{\frown}{xx} - \bar{v}_{\mathrm{Y}}\,.\,\overset{\frown}{xy} - \bar{v}_{\mathrm{H}}\,.\,\overset{\frown}{xh}. \tag{7·14}$$

Now, if we added to the plane, which we may imagine as square, five other planes, also moving with the fluid to form at one instant a unit cube; then we see that the rate of increase of molar kinetic energy in the moving, distorting, swelling cube will instantaneously be

$$\frac{\partial}{\partial x}(\bar{v}_{\mathrm{X}}\,.\,\overset{\frown}{xx} + \bar{v}_{\mathrm{Y}}\,.\,\overset{\frown}{xy} + \bar{v}_{\mathrm{H}}\,.\,\overset{\frown}{xh}) + \frac{\partial}{\partial y}(\bar{v}_{\mathrm{X}}\,.\,\overset{\frown}{yx} + \bar{v}_{\mathrm{Y}}\overset{\frown}{yy} + \bar{v}_{\mathrm{H}}\overset{\frown}{yh})$$
$$+\frac{\partial}{\partial h}(\bar{v}_{\mathrm{X}}\,.\,\overset{\frown}{hx} + \bar{v}_{\mathrm{Y}}\overset{\frown}{hy} + \bar{v}_{\mathrm{H}}\overset{\frown}{hh}). \tag{7·15}$$

Since the mass of the cube is ρ and does not change as the cube swells, the expression (7·16) must be equal to

$$\rho\,\frac{\bar{\mathrm{D}}}{\bar{\mathrm{D}}t}\{\tfrac{1}{2}(v_{\mathrm{X}}{}^2 + v_{\mathrm{Y}}{}^2 + v_{\mathrm{H}}{}^2)\}, \tag{7·16}$$

where $\bar{\mathrm{D}}$ denotes a differentiation following the mean motion. This gives the decrease in the total molar kinetic energy. We want the part of it associated with the eddies, separated from that associated with the mean wind. But the changes which we have been considering are between the cube and fluid touching it, so that they concern only the relative velocity of the cube and its surroundings. Therefore without loss of generality, we may take $\bar{v}_{\mathrm{X}}$, $\bar{v}_{\mathrm{Y}}$, $\bar{v}_{\mathrm{H}}$ as vanishing at the centre of the cube. Then the energy associated with the mean motion vanishes, leaving only the part in Θ. So (7·15) when equated to (7·16) yields

$$\left.\begin{array}{l} \overset{\frown}{xx}\,\dfrac{\partial\bar{v}_{\mathrm{X}}}{\partial x} + \overset{\frown}{xy}\,\dfrac{\partial\bar{v}_{\mathrm{Y}}}{\partial x} + \overset{\frown}{xh}\,\dfrac{\partial\bar{v}_{\mathrm{H}}}{\partial x} \\[2ex] \overset{\frown}{yx}\,\dfrac{\partial\bar{v}_{\mathrm{X}}}{\partial y} + \overset{\frown}{yy}\,\dfrac{\partial\bar{v}_{\mathrm{Y}}}{\partial y} + \overset{\frown}{yh}\,\dfrac{\partial\bar{v}_{\mathrm{H}}}{\partial y} \\[2ex] \overset{\frown}{hx}\,\dfrac{\partial\bar{v}_{\mathrm{X}}}{\partial h} + \overset{\frown}{hy}\,\dfrac{\partial\bar{v}_{\mathrm{Y}}}{\partial h} + \overset{\frown}{hh}\,\dfrac{\partial\bar{v}_{\mathrm{H}}}{\partial h} \end{array}\right\} = \rho\,\frac{\bar{\mathrm{D}}}{\bar{\mathrm{D}}t}\,\Theta. \tag{7·17}$$

The first member is Reynolds' Activity, formed of the products of the eddy-stresses into the corresponding components of mean strain. We have arrived at it by a proof which differs from Reynolds' in that we have :—

(i) Supposed the fluid to be compressible.

(ii) Done away with the rigid envelope at which he made all the velocities to vanish, and have replaced it by certain assumptions as to the approximate vanishing of various means. Just as ordinary thermodynamics is correct because the number of molecules is enormous, so eddy-thermodynamics is an approximation which improves as the number of eddies increases.

In so far as Reynolds' Activity depends upon distortion, we have already dealt with it in Sections II and V above. Let us now suppose that the rates-of-mean-shearing are zero, and let us examine the remaining part due to the expansion. Accordingly, (7·17) will be limited here to

$$\widehat{xx}\,\frac{\partial \bar{v}_{\mathrm{X}}}{\partial x}+\widehat{yy}\,\frac{\partial \bar{v}_{\mathrm{Y}}}{\partial y}+\widehat{hh}\,\frac{\partial \bar{v}_{\mathrm{H}}}{\partial h}=\rho\,\frac{\bar{\mathrm{D}}\Theta}{\bar{\mathrm{D}}t}. \tag{7·18}$$

Now observations by G. I. Taylor and by the author[*] have shown that, except in the first few metres above the surface, $\widehat{xx}=\widehat{yy}=\widehat{hh}$, at least roughly. In other words, there is a tendency to equi-partition of energy between the three components of velocity. For simplicity, let us assume this to be the case, so that from (7·2)

$$\widehat{xx}=\widehat{yy}=\widehat{hh}=-\wp. \tag{7·19}$$

Then from (7·18)

$$\wp\left\{\frac{\partial \bar{v}_{\mathrm{X}}}{\partial x}+\frac{\partial \bar{v}_{\mathrm{Y}}}{\partial y}+\frac{\partial \bar{v}_{\mathrm{H}}}{\partial h}\right\}=-\rho\,\frac{\bar{\mathrm{D}}\Theta}{\bar{\mathrm{D}}t}. \tag{7·20}$$

But by the continuity of mass

$$\frac{\partial \bar{v}_{\mathrm{X}}}{\partial x}+\frac{\partial \bar{v}_{\mathrm{Y}}}{\partial y}+\frac{\partial \bar{v}_{\mathrm{H}}}{\partial h}=-\frac{\bar{\mathrm{D}}}{\bar{\mathrm{D}}t}(\log\rho), \tag{7·21}$$

therefore from (7·20) and (7·21)

$$\wp\,\frac{\bar{\mathrm{D}}}{\bar{\mathrm{D}}t}\log\rho=\rho\,\frac{\bar{\mathrm{D}}\Theta}{\bar{\mathrm{D}}t}, \tag{7·22}$$

or, using (7·5) and transposing

$$\frac{\bar{\mathrm{D}}}{\bar{\mathrm{D}}t}\left\{\tfrac{2}{3}\log\rho-\log\Theta\right\}=0, \tag{7·23}$$

or $\dfrac{\rho^{2/3}}{\Theta}$ is constant following the mean motion.

That is exactly like the adiabatic equation for a gas having a temperature Θ and a ratio of specific heats equal to 5/3—like mercury vapour, krypton, and other monatomic gases.

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[*] 'Phil. Trans.,' A, 1920.

One is tempted to call Θ the "eddy-temperature," but it is perhaps best to avoid this term, for Θ has different dimensions, and so cannot be expressed in degrees on a thermometer. It is correctly called "eddy-heat-per-mass."

We are thus led to the conception of a "potential eddy-heat-per-mass," defined as

$$\Theta\,(\rho_i/\rho)^{2/3}, \tag{7·25}$$

where ρ_i is some standard density.

In arriving at (7·14), we ignored the fact that the molecules do not all move with the velocity v_X, v_Y, v_H, which we attribute to the fluid at a point. But these molecular motions are the cause of the ordinary pressure p. By a method, closely analogous to that by which (7·14) and (7·15) are obtained, it can be shown that (7·14) should be increased by $-v_X p$ and (7·15) by

$$\frac{\partial}{\partial x}(v_X p)+\frac{\partial}{\partial y}(v_Y p)+\frac{\partial}{\partial h}(v_H p)+\text{terms depending on molecular viscosity.}$$

These in turn lead to the lowering of the *ordinary* temperature at a point. But all that is well understood, and our simplest plan is to leave out p from all the equations, and to expect no result relating to ordinary cooling.

Similarly, with regard to gravity. That has been left out. If it had been included, we should have had to consider the mean flux of gravitational energy over a plane moving with the mean motion. The flux will vanish if

$$\overline{\rho' v_H'} = 0, \tag{7·26}$$

that is to say, if convection can be neglected. But having already dealt with convection in Sections IV and V, we may omit it here. Thus the increase of molar-kinetic and of gravitational energy in the cube is still given by (7·15). But, in place of (7·16), we shall have

$$\rho\,\frac{\bar{D}}{\bar{D}t}\{\psi+\tfrac{1}{2}(v_X{}^2+v_Y{}^2+v_H{}^2)\}, \tag{7·27}$$

where ψ is the gravity potential.

It is not now permissible to suppose v_H zero at the centre of the moving cube, since v_H must be relative to the attracting earth. So the first member of (7·17) must be increased by

$$\bar{v}_H\left\{\frac{\partial\overparen{xh}}{\partial x}+\frac{\partial\overparen{yh}}{\partial y}+\frac{\partial\overparen{hh}}{\partial h}\right\}, \tag{7·28}$$

while the second member of the same equation is increased by

$$\rho\,\frac{\bar{D}}{\bar{D}t}\{\psi+\tfrac{1}{2}\bar{v}_H{}^2\}. \tag{7·29}$$

But these two increases balance one another, on account of the dynamical equation. Therefore (7·17) is correct also when gravity is present.

The foregoing theory, which states that the eddy-heat-per-mass is diminished by a mean expansion, may be expected to have some application to the following natural phenomena: (i) turbulent winds flowing up mountain sides; (ii) numerous small eddies carried together upwards in some larger circulation, such as that made visible by cumulus or thunder cloud.

But on account of the assumption (7·11) the theory does not apply to the case in which the small eddies wander individually from crowded to roomy regions.

VIII. *Diffusion of Eddying Energy.* (Revised May 11, 1920.)

Lieut.-Col. A. Ogilvie* describes flying over the Nile in a wind of 13 metres/sec.: "towards 10 o'clock or so the river appeared like a sheet of glass, but a little later, when the sun began to heat the ground, one saw ripples coursing over the surface of the river," and after half-an-hour or so the gusts reached the aviators at a height of about 2/3 km.

Capt. C. K. M. Douglas† also writes of "rising turbulence" as of something commonly experienced. These observations fit in with the theory of Section V to the effect that turbulence usually originates near the ground. According to what law then does it diffuse? Two different processes may go on at the same time. Eddies may wander individually from places where they are crowded to places where they are rare. We may speak of this as a *true* diffusion of eddy-heat-per-mass. Or large whirls, such as those indicated by cumuli, may lift several cubic kilometres of air containing thousands of smaller eddies. This might be called a large-eddy-diffusion of small-eddy-heat-per-mass. Let us discuss this first.

Small-scale-Eddy-heat Carried up by Larger Eddies.

Can it, for instance, be fitted into the following form of diffusion equation?

$$\frac{\partial \chi}{\partial t} = -\frac{\partial}{\partial p}\left(\xi_1 \frac{\partial \chi}{\partial p}\right), \tag{8·1}$$

where ξ_1 is some unknown quantity which is not zero when $\partial\chi/\partial p = 0$. For this to be a possible form χ must satisfy the following conditions.‡

1. χ must be carried along with the moving air. (8·2)
2. χ must be unaltered by the expansion or contraction of the air with which it moves. (8·3)

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* 'Aeronautical Journal,' p. 415, July, 1919.

† 'J. Scott. Met. Soc.,' vol. 17.

‡ Taken with revision from 'Roy. Soc. Proc.,' A, vol. 96, pp. 10, 11 (1919).

And if dm be an element of mass and $\int \chi dm$ be taken over a definite portion of air, then

3. $\int \chi dm$ must be unchanged by internal rearrangement of the portion at constant pressure. (8·4)
4. $\int \chi dm$ must be unchanged by delay. (8·5)

May we put for χ the "potential-eddy-heat-per-mass" discussed in Section VII? That would satisfy (8·2), (8·3), (8·4). Condition (8·5) is not at all satisfied unless we treat the diffusion-process as supplemental to the changes indicated in (5·2) but with this understanding (8·5), and therefore also (8·1), would be satisfied if

$$\chi = \text{potential-eddy-heat-per-mass} = \Theta \left(\frac{\rho i}{\rho}\right)^{2/3},$$

$$= \left(\frac{\rho i}{\rho}\right)^{2/3} \tfrac{1}{2}\,\overline{(v_{\mathrm{X}}'^2 + v_{\mathrm{Y}}'^2 + v_{\mathrm{H}}'^2)},$$

where Θ is the "eddy-heat-per-mass" and ρi is the standard density adopted for the purposes of definition.

The *true diffusion of eddy-heat* bears the same kind of relation to the convection of small eddies with cumuli as molecular conduction of ordinary heat bears to eddy-conduction of the same. We have already encountered in (7·11) an expression giving the mean rate at which energy diffuses across unit area of a plane perpendicular to the x—axis, in the form

$$\frac{1}{\mathrm{A}} \int \tfrac{1}{2} \rho \,(v_{\mathrm{X}}'^2 + v_{\mathrm{Y}}'^2 + v_{\mathrm{H}}'^2)\, v_{\mathrm{X}}'\, d\mathrm{A},$$

but it is required to transform this into another applicable to observations.

Bakerian Lecture: *Nuclear Constitution of Atoms.*

By Sir E. Rutherford, F.R.S., Cavendish Professor of Experimental Physics, University of Cambridge.

(Received June 3,—Lecture delivered June 3, 1920.)

Introduction.—The conception of the nuclear constitution of atoms arose initially from attempts to account for the scattering of α-particles through large angles in traversing thin sheets of matter.* Taking into account the large mass and velocity of the α-particles, these large deflexions were very remarkable, and indicated that very intense electric or magnetic fields exist within the atom. To account for these results, it was found necessary to assume† that the atom consists of a charged massive nucleus of dimensions very small compared with the ordinarily accepted magnitude of the diameter of the atom. This positively charged nucleus contains most of the mass of the atom, and is surrounded at a distance by a distribution of negative electrons equal in number to the resultant positive charge on the nucleus. Under these conditions, a very intense electric field exists close to the nucleus, and the large deflexion of the α-particle in an encounter with a single atom happens when the particle passes close to the nucleus. Assuming that the electric forces between the α-particle and the nucleus varied according to an inverse square law in the region close to the nucleus, the writer worked out the relations connecting the number of α-particles scattered through any angle with the charge on the nucleus and the energy of the α-particle. Under the central field of force, the α-particle describes a hyperbolic orbit round the nucleus, and the magnitude of the deflection depends on the closeness of approach to the nucleus. From the data of scattering of α-particles then available, it was deduced that the resultant charge on the nucleus was about $\frac{1}{2}Ae$, where A is the atomic weight and e the fundamental unit of charge. Geiger and Marsden‡ made an elaborate series of experiments to test the correctness of the theory, and confirmed the main conclusions. They found the nucleus charge was about $\frac{1}{2}Ae$, but, from the nature of the experiments, it was difficult to fix the actual value within about 20 per cent. C. G. Darwin§ worked out completely the deflexion of the α-particle and of the nucleus, taking into account the mass of the latter, and showed that the scattering experiments of Geiger and Marsden could not be reconciled with any law of central force, except the inverse square. The nuclear constitution of the atom was thus very strongly supported by the experiments on scattering of α-rays.

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* Geiger and Marsden, 'Roy. Soc. Proc.,' A, vol. 82, p. 495 (1909).

† Rutherford, 'Phil. Mag.,' vol. 21, p. 669 (1911); vol. 27, p. 488 (1914).

‡ Geiger and Marsden, 'Phil. Mag.,' vol. 25, p. 604 (1913).

§ Darwin, 'Phil. Mag.,' vol. 27, p. 499 (1914).

Since the atom is electrically neutral, the number of external electrons surrounding the nucleus must be equal to the number of units of resultant charge on the nucleus. It should be noted that, from the consideration of the scattering of X-rays by light elements, Barkla* had shown, in 1911, that the number of electrons was equal to about half the atomic weight. This was deduced from the theory of scattering of Sir J. J. Thomson, in which it was assumed that each of the external electrons in an atom acted as an independent scattering unit.

Two entirely different methods had thus given similar results with regard to the number of external electrons in the atom, but the scattering of α-rays had shown in addition that the positive charge must be concentrated on a massive nucleus of small dimensions. It was suggested by Van den Broek† that the scattering of α-particles by the atoms was not inconsistent with the possibility that the charge on the nucleus was equal to the atomic number of the atom, *i.e.*, to the number of the atom when arranged in order of increasing atomic weight. The importance of the atomic number in fixing the properties of an atom was shown by the remarkable work of Moseley‡ on the X-ray spectra of the elements. He showed that the frequency of vibration of corresponding lines in the X-ray spectra of the elements depended on the square of a number which varied by unity in successive elements. This relation received an interpretation by supposing that the nuclear charge varied by unity in passing from atom to atom, and was given numerically by the atomic number. I can only emphasise in passing the great importance of Moseley's work, not only in fixing the number of possible elements, and the position of undetermined elements, but in showing that the properties of an atom were defined by a number which varied by unity in successive atoms. This gives a new method of regarding the periodic classification of the elements, for the atomic number, or its equivalent the nuclear charge, is of more fundamental importance than its atomic weight. In Moseley's work, the frequency of vibration of the atom was not exactly proportional to N, where N is the atomic number, but to $(N-a)^2$, where a was a constant which had different values, depending on whether the K or L series of characteristic radiations were measured. It was supposed that this constant depended on the number and position of the electrons close to the nucleus.

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* Barkla, 'Phil. Mag.,' vol. 21, p. 648 (1911).

† Van den Broek, 'Phys. Zeit.,' vol. 14, p. 32 (1913).

‡ Moseley, 'Phil. Mag.,' vol. 26, p. 1024 (1913); vol. 27, p. 703 (1914).

Charge on the Nucleus.—The question whether the atomic number of an element is the actual measure of its nuclear charge is a matter of such fundamental importance that all methods of attack should be followed up. Several researches are in progress in the Cavendish Laboratory to test the accuracy of this relation. The two most direct methods depend on the scattering of swift α- and β-rays. The former is under investigation, using new methods, by Mr. Chadwick, and the latter by Dr. Crowther. The results so far obtained by Mr. Chadwick strongly support the identity of the atomic number with the nuclear charge within the possible accuracy of experiment, viz., about 1 per cent.

It thus seems clear that we are on firm ground in supposing that the nuclear charge is numerically given by the atomic number of the element. Incidentally, these results, combined with the work of Moseley, indicate that the law of the inverse square holds with considerable accuracy in the region surrounding the nucleus. It will be of great interest to determine the extent of this region, for it will give us definite information as to the distance of the inner electrons from the nucleus. A comparison of the scattering of slow and swift β-rays should yield important information on this point. The agreement of experiment with theory for the scattering of α-rays between 5° and 150° shows that the law of inverse square holds accurately in the case of a heavy element like gold for distances between about 36×10^{-12} cm. and 3×10^{-12} cm. from the centre of the nucleus. We may consequently conclude that few, if any, electrons are present in this region.

An α-particle in a direct collision with a gold atom of nuclear charge 79 will be turned back in its path at a distance of 3×10^{-12} cm., indicating that the nucleus may be regarded as a point charge even for such a short distance. Until swifter α-particles are available for experiment, we are unable in the case of heavy elements to push further the question of dimensions of heavy atoms. We shall see later, however, that the outlook is more promising in the case of lighter atoms, where the α-particle can approach closer to the nucleus.

It is hardly necessary to emphasise the great importance of the nuclear charge in fixing the physical and chemical properties of an element, for obviously the number and the arrangements of the external electrons on which the great majority of the physical and chemical properties depend, is conditioned by the resultant charge on the nucleus. It is to be anticipated theoretically, and is confirmed by experiment, that the actual mass of the nucleus exercises only a second order effect on the arrangement of the external electrons and their rates of vibration.

It is thus quite possible to imagine the existence of elements of almost identical physical and chemical properties, but which differ from one another in mass, for, provided the resultant nuclear charge is the same, a number of possible stable modes of combination of the different units which make up a complex nucleus may be possible. The dependence of the properties of an atom on its nuclear charge and not on its mass thus offers a rational explanation of the existence of isotopes in which the chemical and physical properties may be almost indistinguishable, but the mass of the isotopes may vary within certain limits. This important question will be considered in more detail later in the paper in the light of evidence as to the nature of the units which make up the nucleus.

The general problem of the structure of the atom thus naturally divides itself into two parts:—

1. Constitution of the nucleus itself.
2. The arrangement and modes of vibration of the external electrons.

I do not propose to-day to enter into (2), for it is a very large subject in which there is room for much difference of opinion. This side of the problem was first attacked by Bohr and Nicholson, and substantial advances have been made. Recently, Sommerfeld and others have applied Bohr's general method with great success in explaining the fine structure of the spectral lines and the complex modes of vibration of simple atoms involved in the Stark effect. Recently, Langmuir and others have attacked the problem of the arrangement of the external electrons from the chemical standpoint, and have emphasised the importance of assuming a more or less cubical arrangement of the electrons in the atom. No doubt each of these theories has a definite sphere of usefulness, but our knowledge is as yet too scanty to bridge over the apparent differences between them.

I propose to-day to discuss in some detail experiments that have been made with a view of throwing light on the constitution and stability of the nuclei of some of the simpler atoms. From a study of radio-activity we know that the nuclei of the radio-active elements consist in part of helium nuclei of charge $2e$. We also have strong reason for believing that the nuclei of atoms contain electrons as well as positively charged bodies, and that the positive charge on the nucleus represents the excess positive charge. It is of interest to note the very different *rôle* played by the electrons in the outer and inner atom. In the former case, the electrons arrange themselves at a distance from the nucleus, controlled no doubt mainly by the charge on the nucleus and the interaction of their own fields. In the case of the nucleus, the electron forms a very close and powerful combination with the positively charged units and, as far as we know, there is a region just outside the nucleus where no electron is in stable equilibrium. While no doubt each of the external electrons acts as a point charge in considering the forces between it and the nucleus, this cannot be the case for the electron in the nucleus itself. It is to be anticipated that under the intense forces in the latter, the electrons are much deformed and the forces may be of a very different character from those to be expected from an undeformed electron, as in the outer atom. It may be for this reason that the electron can play such a different part in the two cases and yet form stable systems.

It has been generally assumed, on the nucleus theory, that electric forces and charges play a predominant part in determining the structure of the inner and outer atom. The considerable success of this theory in explaining fundamental phenomena is an indication of the general correctness of this point of view. At the same time if the electrons and parts composing the nucleus are in motion, magnetic fields must arise which will have to be taken into account in any complete theory of the atom. In this sense the magnetic fields are to be regarded as a secondary rather than a primary factor, even though such fields may be shown to have an important bearing on the conditions of equilibrium of the atom.

Dimensions of Nuclei.

We have seen that in the case of atoms of large nuclear charge the swiftest α-particle is unable to penetrate to the actual structure of the nucleus so that it is possible to give only a maximum estimate of its dimensions. In the case of light atoms, however, when the nucleus charge is small, there is so close an approach during a direct collision with an α-particle that we are able to estimate its dimensions and form some idea of the forces in operation. This is best shown in the case of a direct collision between an α-particle and an atom of hydrogen. In such a case, the H atom is set in such swift motion that it travels four times as far as the colliding α-particle and can be detected by the scintillation produced on a zinc sulphide screen.* The writer† has shown that these scintillations are due to hydrogen atoms carrying unit positive charge recoiling with the velocity to be expected from the simple collision theory, viz., 1·6 times the velocity of the α-particle. The relation between the number and velocity of these H atoms is entirely different from that to be expected if the α-particle and H atom are regarded as point charges for the distances under consideration. The result of the collision with swift α-particles is to produce H atoms which have a narrow range of velocity, and which travel nearly in the direction of the impinging particles. It was deduced that the law of inverse squares no longer holds when the nuclei approach to within a distance of 3×10^{-13} cm. of each other. This is an indication that the nuclei have dimensions of this order of magnitude and that the forces between the nuclei vary very rapidly in magnitude and in direction for a distance of approach comparable with the diameter of the electron as ordinarily calculated. It was pointed out that in such close encounters there were enormous forces between the nuclei, and probably the structure of the nuclei was much deformed during the collision. The fact that the helium nucleus, which may be supposed to consist of four H atoms and two electrons, appeared to survive the collision is an indication that it must be a highly stable structure. Similar results* were observed in the collision between α-particles and atoms of nitrogen and oxygen for the recoil atoms appeared to be shot forward mainly in the direction of the α-particles and the region where special forces come into play is of the same order of magnitude as in the case of the collision of an α-particle with hydrogen.

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* Marsden, 'Phil. Mag.,' vol. 27, p. 824 (1914).

† Rutherford, 'Phil. Mag.,' vol. 37, I and II, pp. 538–571 (1919).

No doubt the space occupied by a nucleus and the distance at which the forces become abnormal increase with the complexity of the nucleus structure. We should expect the H nucleus to be the simplest of all and, if it be the positive electron, it may have exceedingly small dimensions compared with the negative electron. In the collisions between α-particles and H atoms, the α-particle is to be regarded as the more complex structure.

The diameter of the nuclei of the light atoms except hydrogen are probably of the order of magnitude 5×10^{-13} cm. and in a close collision the nuclei come nearly in contact and may possibly penetrate each other's structure. Under such conditions, only very stable nuclei would be expected to survive the collision and it is thus of great interest to examine whether evidence can be obtained of their disintegration.

Long Range Particles from Nitrogen.

In previous papers, *loc. cit.*, I have given an account of the effects produced by close collisions of swift α-particles with light atoms of matter with the view of determining whether the nuclear structure of some of the lighter atoms could be disintegrated by the intense forces brought into play in such close collisions. Evidence was given that the passage of α-particles through dry nitrogen gives rise to swift particles which closely resembled in brilliancy of the scintillations and distance of penetration hydrogen atoms set in motion by close collision with α-particles. It was shown that these swift atoms which appeared only in dry nitrogen and not in oxygen or carbon dioxide could not be ascribed to the presence of water vapour or other hydrogen material, but must arise from the collision of α-particles with nitrogen atoms. The number of such scintillations due to nitrogen was small, viz., about 1 in 12 of the corresponding number in hydrogen, but was two to three times the number of natural scintillations from the source. The number observed in nitrogen was on an average equal to the number of scintillations when hydrogen at about 6 cm. pressure was added to oxygen or carbon dioxide at normal pressure.

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* Rutherford, 'Phil. Mag.,' vol. 37, III, p. 571 (1919).

While the general evidence indicated that these long range atoms from nitrogen were charged atoms of hydrogen, the preliminary experiments to test the mass of the particles by bending them in a strong magnetic field yielded no definite results.

From the data given in my previous paper (*loc. cit.*) several theories could be advanced to account for these particles. The calculated range of a singly charged atom set in motion by a close collision with an α-particle of range R cm. in air was shown to be for

Mass 1	....	Range 3·91 R
„ 2	....	„ 4·6 R
„ 3	....	„ 5·06 R
„ 4	....	„ 4·0 R

On account of the small number and weakness of the scintillations under the experimental conditions, the range of the swift atoms from nitrogen could not be determined with sufficient certainty to decide definitely between any of these possibilities. The likelihood that the particles were the original α-particles which had lost one of their two charges, *i.e.*, atoms of charge 1 and mass 4, was suggested by me to several correspondents, but there appeared to be no obvious reason why nitrogen, of all the elements examined, should be the only one in which the passage of a swift α-particle led to the capture of a single electron.

If, however, a sufficient number of scintillations could be obtained under the experimental conditions, there should be no inherent difficulty in deciding between the various possibilities by examining the deflexion of the swift atoms by a magnetic field. The amount of deflexion of charged atoms in a magnetic field perpendicular to the direction of flight is proportional to e/mu. Assuming that the particles were liberated by a direct collision with an α-particle, the relative values of this quantity for different recoiling masses are easily calculated. Taking values MV/E for the α-particle as unity, the corresponding values of mu/e for atoms of charge 1 and mass 1, 2, 3, and 4 are 1·25, 0·75, 0·58, and 0·50 respectively. Consequently the H atoms should be more bent than the α-particles which produced them while the atoms of mass 2 or 3, or 4 would be more difficult to deflect than the parent α-particle.

On my arrival in Cambridge, this problem was attacked in several ways. By the choice of objectives of wide aperture, the scintillations were increased in brilliancy and counting thus made easier. A number of experiments were also made to obtain more powerful sources of radiation with the radium at my command, but finally it was found best, for reasons which need not be discussed here, to obtain the active source of radiation of radium C in the manner described in my previous paper. After a number of observations with solid nitrogen compounds, described later, a simple method was finally devised to estimate the mass of the particle by the use of nitrogen in the gaseous state. The use of the gas itself for this purpose had several advantages over the use of solid nitrogen compounds, for not only was the number of scintillations greater, but the absence of hydrogen or other hydrogen compounds could be ensured.

The arrangement finally adopted is shown in fig. 1. The essential point lay in the use of wide slits, between which the α-particles passed. Experiment showed that the ratio of the number of scintillations on the screen arising from the gas to the number of natural scintillations from the source, increased rapidly with increased depth of the slits. For plates 1 mm. apart this ratio was less than unity, but for slits 8 mm. apart the ratio had a value 2 to 3. Such a variation is to be anticipitated on theoretical grounds if the majority of the particles are liberated at an angle with the direction of the incident α-particles.

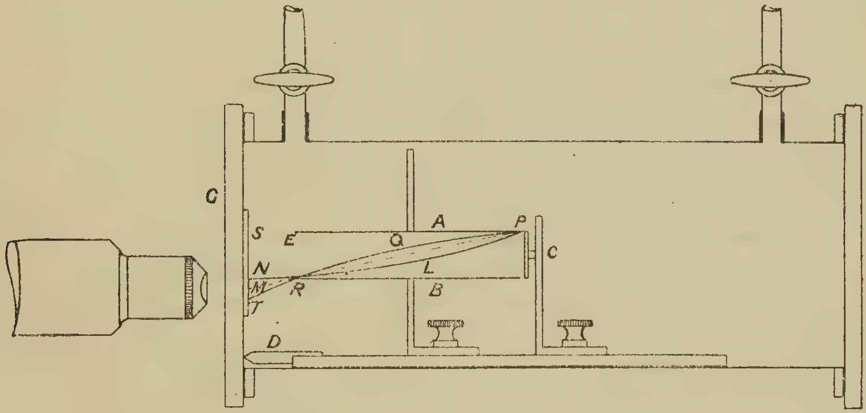

Fig. 1.

The horizontal slits A, B were 6·0 cm. long, 1·5 cm. wide, and 8 mm. deep, with the source, C of the active deposit of radium placed at one end and the zinc sulphide screen near the other. The carrier of the source and slits were placed in a rectangular brass box, through which a current of dry air or other gas was continuously passed to avoid the danger of radio-active contamination. The box was placed between the poles of a large electromagnet, so that the uniform field was parallel to the plane of the plates and perpendicular to their length. A distance piece, D, of length 1·2 cm., was added between the source and end of the slits, in order to increase the amount of deflexion of the radiation issuing from the slits. The zinc sulphide screen, S, was placed on a glass plate covering the end of the box. The distance between the source and the screen was 7·4 cm. The recoil atoms from oxygen or nitrogen of range 9 cm. could be stopped by inserting an aluminium screen of stopping power about 2 cm. of air placed at the end of the slits.

With such deep slits it was impossible to bend the wide beam of radiation to the sides, but the amount of deflexion of the radiation issuing near the bottom of the slit was measured. For this purpose it was essential to observe the scintillations at a fixed point of the screen near M. The method of fixing the position of the counting microscope was as follows: The source, C, was placed in position, and the air exhausted to a pressure of a few centimetres. Without the field, the bottom edge of the beam was fixed by the straight line PM cutting the screen at M. The microscope was adjusted so that the boundary line of scintillations appeared above the horizontal cross wire in the microscope, marking the centre of the field.

On exciting the magnet to bend the rays upward (called the + field), the path of the limiting α-particles is marked by the curve PLRN cutting the screen at N, so that the boundary of the scintillations appears to be displaced downwards in the field of view. On reversing the field (called the − field), the path of the limiting α-particle PQRT cuts the screen at T, and the band of scintillations appears to be bent upwards. The strength of the magnetic field was adjusted so that, with a negative field, the scintillations were observed all over the screen, while, with a positive field, they were mainly confined below the cross wire. The appearance in the field of view of the microscope for the two fields is illustrated in fig. 2, where the dots represent approximately the density of distribution of the scintillations. The horizontal boundaries of the field of view were given by a rectangular opening in a plate fixed in the

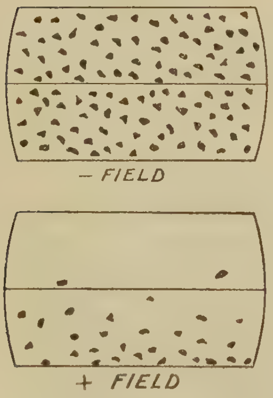

Fig. 2.

position of the cross wires. A horizontal wire, which bisected the field of view, was visible under the conditions of counting, and allowed the relative numbers of scintillations in the two halves of the field to be counted if required. Since the number of scintillations in the actual experiments with nitrogen was much too small to mark directly the boundary of the scintillations, in order to estimate the bending of the rays, it was necessary to determine the ratio of the number of scintillations with the + and − field.

The position of the microscope and the strength of the magnetic field were in most experiments so adjusted that this ratio was about one-third. Preliminary observations showed that this ratio was sensitive to changes of the field and it thus afforded a suitable method for estimating the relative bending of any radiations under examination.

After the position of the microscope was fixed, air was let in, and a continuous flow of dry air maintained through the apparatus. The absorbing screen was introduced at E to stop the atoms from N and O of range 9 cm. The number of scintillations was then systematically counted for the two directions of the field, and a correction, if required, made for any slight radio-active contamination of the screen. The deflexion due to the unknown radiation was directly compared with that produced by a known radiation of α-rays. For this purpose, after removal of the source and absorbing screen, a similar plate, coated with a weak distribution of the active deposit of thorium, was substituted for the radium source. The α-particles from thorium C of range 8·6 cm. produced bright scintillations in the screen after traversing the 7·4 cm. of air in their path. The ratio of the number of scintillations with + and − fields was determined as before.

An example of such comparison is given below. For a current of 4·0 amp. through the electromagnet, the ratio for particles from nitrogen was found to be 0·33. The corresponding ratio for α-particles from thorium C was 0·44 for a current of 4 amp. and 0·31 for a current of 5 amp. It is thus seen that on the average, the particles from nitrogen are more bent in a given field than the α-particles from thorium C. In order, however, to make a quantitative comparison, it is necessary to take into account the reduction in velocity of the radiations in passing through the air. The value mu/e for the α-ray of range 8·6 cm. from thorium C is known to be $4{\cdot}28 \times 10^5$. Since the rays pass through 7·4 cm. of air in a uniform field before striking the screen, it can be calculated that the actual deflection corresponds to α-rays in a vacuum for which $mu/e = 3{\cdot}7 \times 10^5$, about. Taking the deflection of the α-particles for a current of 4·8 amp. to be the same as for the nitrogen particles for a field of 4 amp.—ratio of fields 1·17—it is seen that the average deflexion of the nitrogen particles under the experimental conditions corresponds to a radiation in a vacuum for which the value of $mu/e = 3{\cdot}1 \times 10^5$.

Bearing in mind that the particles under examination are produced throughout the volume of the gas between the slits, and that their distribution is unknown, and also that the particles are shot forward on an average at an angle with the incident α-particles, the experimental data are quite insufficient to calculate the average value of mu/e to be expected under the experimental conditions for any assumed mass of projected particles. It seems probable that the majority of the particles which produce scintillations are generated in the first few centimetres of the air next the source. The actual deflection of a given particle by the magnetic field will depend on the distance of its point of origin from the source. These factors will obviously tend to make the average deflection of the particles to appear less than if they were all expelled with constant velocity from the source itself. Assuming that the correction for reduction of velocity of the long range particles in traversing the gas is 10 per cent., the average value of mu/e is about $3{\cdot}4 \times 10^5$. Since the value of MV/E for the α-particle from radium C is $3{\cdot}98 \times 10^5$, it is seen that under the experimental conditions the average value of mu/e for the nitrogen particles is less than that of the α-particles which produce them.

From the data given earlier in the paper, this should only be true if the particles are comparable in mass with an atom of hydrogen, for singly charged particles of mass 2, 3, or 4 should suffer less deflexion than the α-particles. For example, if we assume that the particles were helium atoms carrying one charge, we should expect them to be deflected to about one-half of the extent of the α-particle. The experimental results thus afford strong presumptive evidence that the particles liberated from nitrogen are atoms of hydrogen.

A far more decisive test, however, can be made by comparing the deflexion of the nitrogen particles with that of H atoms under similar conditions. For this purpose, a mixture of about one volume of hydrogen to two of carbon dioxide was stored in a gas-holder and circulated in place of air through the testing apparatus. The proportions of the two gases were so adjusted that the stopping power of the mixture for α-rays was equal to that of air. Under these conditions, the H atoms, like the nitrogen particles, are produced throughout the volume of the gas, and probably the relative distribution of H atoms along the path of the α-rays is not very different from that of the nitrogen particles under examination. If the nitrogen particles are H atoms, we should expect the average deflexion to be nearly the same as for the H atoms liberated from the hydrogen mixture. A number of careful experiments showed that the ratio of the number of scintillations in + and − fields of equal value was so nearly identical in the two cases that the experiments were unable to distinguish between them. Since the two experiments were carried out under as nearly as possible identical conditions, the equality of the ratio shows that the long range particles liberated from nitrogen are atoms of hydrogen. The possibility that the particles may be of mass 2, 3, or 4 is definitely excluded.

In a previous paper I have given evidence that the long range particles observed in dry air and pure nitrogen must arise from the nitrogen atoms themselves. It is thus clear that some of the nitrogen atoms are disintegrated by their collision with swift α-particles and that swift atoms of positively charged hydrogen are expelled. It is to be inferred that the charged atom of hydrogen is one of the components of which the nucleus of nitrogen is built up.

While it has long been known that helium is a product of the spontaneous transformation of some of the radio-active elements, the possibility of disintegrating the structure of stable atoms by artificial methods has been a matter of uncertainty. This is the first time that evidence has been obtained that hydrogen is one of the components of the nitrogen nucleus.

It should be borne in mind that the amount of disintegration effected in nitrogen by the particles is excessively small, for probably on an average only one α-particle in about 300,000 is able to get near enough to the nitrogen nucleus to liberate the atom of hydrogen with sufficient energy to be detected by the scintillation method. Even if the whole α-radiation from 1 gramme of radium were absorbed in nitrogen gas, the volume of hydrogen set free would be only about 1/300000 of the volume of helium due to the collected α-particles, viz., about 5×10^{-4} cub. mm. per year. It may be possible that the collision of an α-particle is effective in liberating the hydrogen from the nucleus without necessarily giving it sufficient velocity to be detected by scintillations. If this should prove to be the case, the amount of disintegration may be much greater than the value given above.

Experiments with Solid Nitrogen Compounds.

A brief account will now be given of experiments with solid nitrogen compounds. Since the liberation of the particle from nitrogen is a purely atomic phenomenon, it was to be expected that similar particles would be liberated from nitrogen compounds in number proportional to the amount of nitrogen. To test this point, and also the nature of the particles, a number of compounds rich in nitrogen were examined. For this purpose

I have employed the following substances, which were prepared as carefully as possible to exclude the presence of hydrogen in any form :—

1. Boron nitride, kindly prepared for me by W. J. Shutt, in Manchester University.

2. Sodium nitride, titanium nitride and para-cyanogen, kindly prepared for me by Sir William Pope and his assistants.

The apparatus used was similar in form to that given in fig. 1, except that the plates were 4 cm. long. By means of a fine gauze, the powdered material was sifted as uniformly as possible on a thin aluminium plate about 2 sq. cm. in area. The weight of the aluminium plate was about 6 mgrm. per square centimetre, and usually about 4 to 5 mgrm. of the material per square centimetre was used. The stopping power of the aluminium plate for α-particles corresponded to about 3·4 cm. of air, and it was usually arranged that the average stopping power of the material was about the same as for the aluminium. In order to make the material adhere tightly to the plate, a layer of alcohol was first brushed on and the material rapidly sifted into position, and the plate then dried.

Experiment showed that no detectable hydrogen contamination was introduced by the use of alcohol in this way. The zinc sulphide screen was placed outside the box close to an aluminium plate of stopping power equal to 5·2 cm. of air which covered an opening in the end of the brass box. The aluminium carrier was then placed in position to cover the end of the slits near the source, care being taken not to shake off any material. The air was exhausted and the number of scintillations on the screen counted.

1. With material facing the source.
2. With plate reversed.

In the former case, the α-particles were fired directly into the material under examination; in the latter case the α-particles only fell on the material when their range was reduced to about half, when their power of liberating swift atoms is much reduced. This method of reversal had the great advantage that no correction was necessary for unequal absorption of the H-particles from the source in different experiments.

In this way it was found that all the nitrogen compounds examined gave a larger number of scintillations in position (1). The nature of these particles was examined by a method similar to that employed in the case of nitrogen and a direct comparison was made of the deflexion of the particles with that of H atoms liberated from a film of paraffin put in place of the nitrogen compound. In all experiments, the particles were found to be deflected to the same degree as H atoms from the paraffin and no trace of particles of mass 2, 3 or 4 was detected.

For films of equal average stopping power for α-rays, it can readily be calculated from Bragg's rule that the relative stopping power of the nitrogen in the compounds is 0·67 for B.N., 0·74 for C_2N_2, 0·40 for titanium nitride, taking the stopping power of sodium nitride as unity. Since the expulsion of long range nitrogen particles must be an atomic phenomenon, it was to be expected that the number of scintillations under the experimental conditions, after correction for the natural effect from the source, should be proportional to the relative values of stopping power given above. The observations with sodium nitride and titanium nitride were very consistent and the number of long range nitrogen particles was in the right proportion and about the same as that to be expected from the experiments with nitrogen gas. On the other hand, boron nitride and para-cyanogen gave between 1·5 and 2 times the number to be expected theoretically. In these experiments every precaution was taken to get rid of hydrogen and water vapour. Before use, the aluminium plates were heated in an exhausted quartz tube in an electric furnace nearly to its melting point to get rid of hydrogen and other gases. The films under examination were kept in a dessicator and heated in the electric furnace just before use and transferred at once to the testing vessel. Several control experiments were made, using preparations not containing nitrogen, viz., pure graphite and silica which had been kindly prepared for me by Sir William Pope. In both of these cases, the number of scintillations observed with the material facing the α-rays was actually less than when the plate was reversed. This showed that some H atoms were liberated by the α-rays from the heated aluminium. The control experiments were thus very satisfactory in showing that H atoms were not present in materials not containing nitrogen. Incidentally, they show that H atoms do not arise in appreciable numbers from carbon, silicon, or oxygen.

The increased effect in boron nitride and para-cyanogen naturally led to the suspicion that these preparations contained some hydrogen although every precaution was taken to avoid such a possibility. In the case of boron nitride there is also the uncertainty whether boron itself emits H atoms. This point has not yet been properly examined. On account of these uncertainties, experiments on solid nitrogen compounds were abandoned for the time, and experiments already described made directly on gaseous nitrogen.

It is of interest to note that a considerable contamination with hydrogen is required to produce the number of H atoms observed in these compounds. In the case of sodium nitride at least 50 c.c. of hydrogen must be present per gram of material. I am inclined to think that the H atoms liberated by the α-rays from sodium nitride is due mainly, if not entirely to the nitrogen, and in the case of para-cyanogen, part of the effect is probably due to the presence of hydrogen or other hydrogen compound. It is hoped to examine this question in more detail later.

Short Range Atoms from Oxygen and Nitrogen.

In addition to the long range H atoms liberated from nitrogen, the passage of α-particles through oxygen as well as through nitrogen gives rise to much more numerous swift atoms, which have a range in air of about 9·0 cm. compared with that of 7·0 cm. for the colliding α-particles. The method of determining the range and number of these atoms has been explained in a previous paper.* It is there shown that these projected atoms arise from the passage of the α-particles through the gas. Just beyond the range of the α-particles from radium C, the scintillations are much brighter than those due to H atoms, and more resemble α-particles.

In the absence of definite information as to the nature of these atoms, it was provisionally assumed that they were atoms of oxygen or nitrogen carrying a single charge set in swift motion by close collisions with α-particles, for the observed range of these particles was in approximate accord with that calculated on these assumptions. At the same time it was pointed out that the agreement of the ranges of the atoms set free in N and O was rather surprising, for it was to be anticipated that the range of the swifter N atoms should be about 19 per cent. greater than for the slower O atoms. The possibility that these swift atoms might prove to be fragments of disintegrated atoms was always present, but up till quite recently, I did not see any method of settling the question.†

As soon as the use of wide slits had proved successful in deciding the nature of the long range particles from nitrogen, experiments were made with the same apparatus and method to test the nature of the short range particles in O and N.

First consider the relative deflexion to be expected for an O atom which is set in motion by a direct impact with an α-particle. The velocity of the O atom after the collision is 2/5 V, where V is the velocity of the incident α-particle. The value of mu/e for the O atom carrying a single charge is easily seen to be 3·1 times that of the α-particle before impact. Consequently the O atom with a single charge should be much more difficult to deflect than the α-particle, and this is the case even if the former carries two charges.

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* Rutherford, 'Phil. Mag.,' vol. 37, III, p. 571 (1919).

† Mr. G. S. Fulcher, of the National Research Council, U.S.A., sent me, in November, 1919, a suggestion that these atoms might prove to be α-particles.

To test these points, the apparatus was the same as that shown in fig. 1. The source was 7·4 cm. distant from the zinc sulphide screen, the end pieces, 1·2 cm. long, being used as before to increase the deflexion of the rays. During an experiment, dried air or oxygen was circulated slowly through the apparatus to avoid radio-active contamination of the screen. In the case of oxygen, the scintillations observed on the screen were due to the O atoms with a small proportion of H atoms from the source. In the case of air, the scintillations on the screen were due partly to N atoms, some O atoms, and H atoms from the source and nitrogen. The actual number of short range N atoms appeared to be less than the number of O atoms under similar conditions.

The position of the microscope was fixed as before to give a convenient ratio for the number of scintillations on reversing the magnetic field. This ratio varied with the position of the microscope, and in the actual experiments had values between 0·2 and 0·4.

It was at once obvious that the atoms from O instead of being *less* deflected than the α-particles, as they should be if they were O atoms, were *more* deflected. This at once excluded the possibility that the atoms from oxygen were actual atoms of oxygen carrying either one or two charges. Since helium is expelled in so many radio-active changes, it might be expected to be one of the components of light atoms, liberated by the intense collision. The deflexion of the atoms from O was, however, much too large to be accounted for in this way. To test this point, at the conclusion of the experiments with oxygen, a plate which had been exposed to thorium emanation was substituted for the radium source, and the bending of the rays of range 8·6 cm. from thorium C was examined in a similar way. If an α-particle were ejected from an O atom near the source, it would be bent like an α-particle of range 9·0 cm.; if produced near the end of the range of α-rays, the amount of bending could not be more than for an α-particle of range 7·0 cm., *i.e.*, about 9 per cent. more than in the first case. Even supposing the particles were liberated uniformly along the path of the α-rays and moved in the same line as the colliding particle, the average bending would not differ by 5 per cent. from that of the α-particle from thorium C. If, as seems probable, some of the atoms are liberated at an angle with the incident particles, the average amount of bending of the beam would be less than the above, and in all probability less than for the α-particles from thorium C. Actually the bending observed was about 20 per cent. greater, showing that the hypothesis that the atoms from O are charged atoms of helium is quite untenable.

If the atoms from O were H atoms, they would be more bent than the α-particles, but would have a maximum range of 28 cm. instead of the

9·0 cm. observed. It thus seemed clear from this evidence that the atom must be of mass intermediate between 1 and 4, while from consideration of the range of the particles and their amount of deflexion it was clear that the atom carried two units of charge.

In order to make a more decisive test, the deflexion of O atoms in a positive and negative field of given value was directly compared with the deflexion of H atoms from a mixture of hydrogen and carbonic acid, in the ratio of about 1 to 2 in volume. In order to absorb completely the O atoms from CO_2, aluminium foil was placed over the zinc sulphide screen, so that the total absorption between the source and screen corresponded to slightly more than 9 cm. of air. In both experiments, the atoms under examination are produced in the gas between the slits, and probably the relative distribution along the path of the α-rays is not markedly different in the two cases.

The ratios for reversing the field in the two experiments were found to be nearly equal; but, as an average of a number of experiments, the H atoms were slightly more bent than the atoms from O. From a number of experiments it was concluded that the difference in deflexion did not on the average amount to more than 5 per cent., although from the nature of the observations it was difficult to fix the difference with any certainty.

From these data and the range of the atoms from O in air, we can deduce the mass of the particle liberated from oxygen.

Let m = mass of the atom from O,
u = its maximum velocity near the source,
E = charge

Let M, V, E be the corresponding values for the incident α-particles and $m'u'e$ the values for the H atoms liberated close to the source.

Taking into account that the particle from O of range 9 cm. is steadily reduced in velocity in passing through the 7·4 cm. of oxygen between the source and screen, it can easily be calculated that its average deflexion by the magnetic field is proportional to $1{\cdot}14\,\mathrm{E}/mu$ in place of E/mu in a vacuum.

In a similar way, the deflexion of the H atom is proportional to $1{\cdot}05\,e/m'u'$, the correction in this case for change of velocity being smaller, and estimated to be about 5 per cent. Now we have seen that the experimental results showed that the atoms from O were bent about 5 per cent. less than the H atoms. Consequently

$$1{\cdot}14\,\mathrm{E}/mu = \frac{1{\cdot}05}{1{\cdot}05}\,e/m'u' = 1{\cdot}25\,\mathrm{E}/mv,$$

or

$$1{\cdot}14\,\mathrm{MV} = 1{\cdot}25\,mu, \tag{1}$$

since it has been calculated and verified by experiment that the deflexion of the H atom in a magnetic field is 1·25 times that of the α-particle which sets it in motion (see Paper II, *loc. cit.*). Also in a previous paper, III, I have given reasons for believing that the range x of mass m and initial velocity u, carrying a double charge, is given by

$$\frac{x}{\mathrm{R}}=\frac{m}{\mathrm{M}}\left(\frac{u}{\mathrm{V}}\right)^3,$$

where R is the range of the α-particle of mass M and velocity V. Since $x = 9·0$ cm. for the atoms from O set in motion by collision with α-particles from radium C of range 7 cm.,

$$\frac{x}{\mathrm{R}} = 1·29,$$

and taking $\mathrm{M} = 4$ $$mu^3 = 5·16\,v^3. \quad (2)$$

A formula of this type has been shown to account for the range of the H atom, and there is every reason to believe it is fairly accurate over such a short difference of range.

From (1) and (2) $$\underline{u} = \underline{1·19\,\mathrm{V}},$$

$$\underline{m} = \underline{3·1}.$$

Considering the difficulty of obtaining accurate data, the value $m = 3·1$ indicates that the atom has a mass about 3 and this value will be taken as the probable value in later discussions.

When air was substituted for oxygen it was not possible to distinguish any difference between the bending of the short range atoms in the two cases. Since the short range atoms from air arise mainly from the nitrogen, we may consequently conclude that the short range atoms liberated by the passage of particles through oxygen or nitrogen consist of atoms of mass 3, carrying a double charge, and initially projected with a velocity 1·19 V, where V is the velocity of the colliding α-particle.

There seems to be no escape from the conclusion that these atoms of mass 3 are liberated from the atoms of oxygen or nitrogen as a result of an intense collision with an α-particle. It is thus reasonable to suppose that atoms of mass 3 are constituents of the structure of the nuclei of the atoms of both oxygen and nitrogen. We have shown earlier in the paper that hydrogen is also one of the constituents of the nitrogen nucleus. It is thus clear that the nitrogen nucleus can be disintegrated in two ways, one by the expulsion of an H atom and the other by the expulsion of an atom of mass 3 carrying two charges. Since now these atoms of mass 3 are five to ten times as numerous as the H atoms, it appears that these two forms of disintegration are independent and not simultaneous. From the rareness of the collisions it is highly improbable that a single atom undergoes both types of disintegration.

Since the particles ejected from O and N are not produced at the source, but along the path of the α-particles, it is difficult to determine their mass and velocity with the precision desired. To overcome this drawback, attempts were made to determine the deflection of O atoms released from a mica plate placed over the source. In consequence of hydrogen in combination in the mica, the H atoms falling on the screen were so numerous compared with the O particles, and their deflexion under the experimental conditions so nearly alike, that it was difficult to distinguish between them.

Energy Considerations.

In close collisions between an α-particle and an atom, the laws of conservation of energy and of momentum appear to hold,* but, in cases where the atoms are disintegrated, we should not necessarily expect these laws to be valid, unless we are able to take into account the change of energy and momentum of the atom in consequence of its disintegration.

In the case of the ejection of a hydrogen atom from the nitrogen nucleus, the data available are insufficient, for we do not know with certainty either the velocity of the H atom or the velocity of the α-particle after the collision.

If we are correct in supposing that atoms of mass 3 are liberated from O and N atoms, it can be easily calculated that there is a slight gain of energy as a result of the disintegration. If the mass is 3 exactly, the velocity of escape of the atom is 1·20 V, where V is the velocity of the impinging α-particle.

Thus, $$\frac{\text{energy of liberated atom}}{\text{energy of } \alpha\text{-particle}} = \frac{3 \times 1{\cdot}44}{4} = 1{\cdot}08,$$

or there is a gain of 8 per cent. in energy of motion, even though we disregard entirely the subsequent motion of the disintegrated nucleus or of the colliding α-particle. This extra energy must be derived from the nitrogen or oxygen nucleus in the same way that the α-particle gains energy of motion in escaping from the radio-active atom.

For the purpose of calculation, consider a direct collision between an α-particle and an atom of mass 3. The velocity of the latter is 8/7 V, where V is the velocity of the α-particle, and its energy is 0·96 of the initial energy of the α-particle. No doubt, in the actual case of a collision with the O or N atom, in which the atom of mass 3 is liberated, the

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* Rutherford, 'Phil. Mag.,' vol. 37, p. 562 (1919).

α-particle comes under the influence of the main field of the nucleus, as well as of that of the part of mass 3 immediately in its path. Under such conditions, it is not to be expected that the α-particle can give 0·96 of its energy to the escaping atom, but the latter acquires additional energy due to the repulsive field of the nucleus.

In our ignorance of the constitution of the nuclei and the nature of the forces in their immediate neighbourhood, it is not desirable to enter into speculations as to the mechanism of the collision at this stage, but it may be possible to obtain further information by a study of the trails of α-particles through oxygen or nitrogen by the well-known expansion method of C. T. R. Wilson. In a previous paper,* I discussed the photograph obtained by Mr. Wilson, in which there is a sudden change of 43° in the direction of the trail, with the appearance of a short spur at the fork. Evidence was given that the relative length of the tracks of the α-particle and of the spur were in rough accord with the view that the spur was due to the recoiling oxygen atom. This is quite probably the case, for the general evidence shows that the atoms of mass 3, after liberation, travel nearly in the direction of the α-particle, and an oblique collision may not result in the disintegration of the atom.

Recently, Dr. Shimizu, of the Cavendish Laboratory, has devised a modification of the Wilson expansion apparatus, in which expansions can be periodically produced several times a second, so that the trails of many particles can be inspected in a reasonable time. Under these conditions, both Shimizu and myself saw on several occasions what appeared to be branching trails of an α-particle in which the lengths of the two tracks were comparable. Eye observations of this kind are too uncertain to regard them with much confidence, so arrangements are being made by Mr. Shimizu to obtain photographs, so that the tracks can be examined in detail at leisure. In this way we may hope to obtain valuable information as to the conditions which determine the disintegration of the atoms, and on the relative energy communicated to the three systems involved, viz., the α-particle, the escaping atom, and the residual nucleus.

So far no definite information is available as to the energy of the α-particle required to produce disintegration, but the general evidence indicates that fast α-particles, of range about 7 cm. in air, are more effective than α-particles of range about 4 cm. This may not be connected directly with the actual energy required to effect the disintegration of the atom itself, but rather to the inability of the slower α-particle under the repulsive field to approach close enough to the nucleus to be effective in disrupting it. Possibly the actual energy required to disintegrate the atom is small compared with the energy of the α-particle.

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* Rutherford, 'Phil. Mag.,' vol. 37, p. 577 (1919).

If this be the case, it may be possible for other agents of less energy than the α-particle to effect the disintegration. For example, a swift electron may reach the nucleus with sufficient energy to cause its disintegration, for it moves in an attractive and not a repulsive field as in the case of the α-particle. Similarly, a penetrating γ-ray may have sufficient energy to cause disintegration. It is thus of great importance to test whether oxygen or nitrogen or other elements can be disintegrated under the action of swift cathode rays generated in a vacuum tube. In the case of oxygen and nitrogen, this could be tested simply by observing whether a spectrum closely resembling helium is given by the gas in the tube, after an intense bombardment of a suitable substance, by electrons. Experiments of this type are being undertaken by Dr. Ishida in the Cavendish Laboratory, every precaution being taken by the heating of the vacuum tube of special glass and electrodes to a high temperature to ensure the removal of any occluded helium which may be initially in the material. Helium has previously been observed by several investigators in vacuum tubes and is known to be released from substances by bombardment with cathode rays. The proof of the actual production of helium in such cases is exceedingly difficult, but the recent improvements in vacuum tube technique may make it easier to give a decisive answer to this important question.

Properties of the new Atom.

We have shown that atoms of mass about 3 carrying two positive charges are liberated by α-particles both from nitrogen and oxygen, and it is natural to suppose that these atoms are independent units in the structure of both gases. Since probably the charged atom during its flight is the nucleus of a new atom without any external electrons, we should anticipate that the new atom when it has gained two negative electrons should have physical and chemical properties very nearly identical with those of helium, but with a mass 3 instead of 4. We should anticipate that the spectrum of helium and this isotope should be nearly the same, but on account of the marked difference in the relative masses of the nuclei, the displacement of the lines should be much greater than in the case of isotopes of heavy elements like lead.

It will be remembered that Bourget, Fabry, and Buisson,[*] from an examination of the width of the lines in the spectrum of nebulæ, conclude that the spectrum arises from an element of atomic mass about 2·7 or 3 in round numbers. It is difficult, however, on modern views to suppose that the spectrum of the so-called "nebulium" can be due to an element of nuclear charge 2 unless the spectrum under the conditions existing in nebulæ are very different from those observed in the laboratory. The possible origin of the spectrum of nebulium has been discussed at length by Nicholson* on quite other lines, and it is not easy at the moment to see how the new atoms from oxygen or nitrogen can be connected with the nebular material.

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[*] Bourget, Fabry and Buisson, 'C. R.,' April 6, May 18 (1914).

Since probably most of the helium in use is derived, either directly or indirectly, from the transformation of radio-active materials, and these, as far as we know, always give rise to helium of mass 4, the presence of an isotope of helium of mass 3 is not likely to be detected in such sources. It would, however, be of great interest to examine whether the isotope may be present in cases where the apparent presence of helium is difficult to connect with radio-active material; for example, in beryl, drawn attention to by Strutt.† This is based on the assumption that the atom of mass 3 is stable. The fact that it survives the intense disturbance of its structure due to a close collision with an α-particle is an indication that it is a structure difficult to disintegrate by external forces.

Constitution of Nuclei and Isotopes.

In considering the possible constitution of the elements, it is natural to suppose that they are built up ultimately of hydrogen nuclei and electrons. On this view the helium nucleus is composed of four hydrogen nuclei and two negative electrons with a resultant charge of two. The fact that the mass of the helium atom 3·997 in terms of oxygen 16 is less than the mass of four hydrogen atoms, viz., 4·032, has been generally supposed to be due to the close interaction of the fields in the nucleus resulting in a smaller electromagnetic mass than the sum of the masses of the individual components. Sommerfeld‡ has concluded from this fact that the helium nucleus must be a very stable structure which would require intense forces to disrupt it. Such a conclusion is in agreement with experiment, for no evidence has been obtained to show that helium can be disintegrated by the swift α-particles which are able to disrupt the nuclei of nitrogen and oxygen. In his recent experiments on the isotopes of ordinary elements Aston§ has shown that within the limit of experimental accuracy the masses of all the isotopes examined are given by whole numbers when oxygen is taken as 16. The only exception is hydrogen, which has a mass 1·008 in agreement with chemical observations. This does not exclude the probability that hydrogen is the ultimate constituent of which nuclei are composed, but indicates that either the grouping of the hydrogen nuclei and electrons is such that the average electromagnetic mass is nearly 1, or, what is more probable, that the secondary units, of which the atom is mainly built up, *e.g.*, helium or its isotope, have a mass given nearly by a whole number when O is 16.

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* Nicholson, 'Roy. Ast. Soc.,' vol. 72, No. 1, p. 49 (1911); vol. 74, No. 7, p. 623 (1914).

† Strutt, 'Roy. Soc. Proc.,' A, vol. 80, p. 572 (1908).

‡ Sommerfeld, 'Atombau und Spektrallinien,' p. 538. Vieweg and Son, 1919.

§ Aston, 'Phil. Mag.,' December, 1919: April and May, 1920.

The experimental observations made so far are unable to settle whether the new atom has a mass exactly 3, but from the analogy with helium we may expect the nucleus of the new atom to consist of three H nuclei and one electron, and to have a mass more nearly 3 than the sum of the individual masses in the free state.

If we are correct in this assumption it seems very likely that one electron can also bind two H nuclei and possibly also one H nucleus. In the one case, this entails the possible existence of an atom of mass nearly 2 carrying one charge, which is to be regarded as an isotope of hydrogen. In the other case, it involves the idea of the possible existence of an atom of mass 1 which has zero nucleus charge. Such an atomic structure seems by no means impossible. On present views, the neutral hydrogen atom is regarded as a nucleus of unit charge with an electron attached at a distance, and the spectrum of hydrogen is ascribed to the movements of this distant electron. Under some conditions, however, it may be possible for an electron to combine much more closely with the H nucleus, forming a kind of neutral doublet. Such an atom would have very novel properties. Its external field would be practically zero, except very close to the nucleus, and in consequence it should be able to move freely through matter. Its presence would probably be difficult to detect by the spectroscope, and it may be impossible to contain it in a sealed vessel. On the other hand, it should enter readily the structure of atoms, and may either unite with the nucleus or be disintegrated by its intense field, resulting possibly in the escape of a charged H atom or an electron or both.

If the existence of such atoms be possible, it is to be expected that they may be produced, but probably only in very small numbers, in the electric discharge through hydrogen, where both electrons and H nuclei are present in considerable numbers. It is the intention of the writer to make experiments to test whether any indication of the production of such atoms can be obtained under these conditions.

The existence of such nuclei may not be confined to mass 1 but may be possible for masses 2, 3, or 4, or more, depending on the possibility of combination between the doublets. The existence of such atoms seems almost necessary to explain the building up of the nuclei of heavy elements; for unless we suppose the production of charged particles of very high velocities it is difficult to see how any positively charged particle can reach the nucleus of a heavy atom against its intense repulsive field.

We have seen that so far the nuclei of three light atoms have been recognised experimentally as probable units of atomic structure, viz.,

$$\overset{+}{H_1}, \quad \overset{++}{X_3}, \quad \overset{++}{He_4},$$

where the subscript represents the mass of the element.

In considering the possible ways in which nuclei can be built up, difficulties at once arise, for many combinations of these units with negative electrons are possible to give an element of the required nuclear charge and mass. In our complete ignorance of the laws of force close to the nuclei, no criterion is available as to the stability or relative probability of the theoretical systems. With the exception of a few elements which can exist in the gaseous state, the possible isotopes of the elements have not yet been settled. When further information is available as to the products of the disintegration of other elements than the two so far examined, and more complete data have been obtained as to the number and mass of the isotopes, it may be possible to deduce approximate rules which may serve as a guide to the mode in which the nuclei are built up from the simpler units. For these reasons it seems premature at this stage to attempt to discuss with any detail the possible structure of even the lighter and presumably less complex atoms. It may, however, be of some interest to give an example to illustrate a possible method of the formation of isotopes in the case of the lighter elements. This is based on the view that probably in many cases a helium nucleus of mass 4 may be substituted in the complex structure for the corresponding nucleus of mass 3 without seriously interfering with the stability of the system. In such a case, the nuclear charge remains unchanged but the masses differ by unity.

For example, take the case of lithium of nuclear charge 3 and atomic mass about 7. It is natural to suppose that the nucleus is composed of helium or its isotope of mass 3 with one binding electron. The three possible combinations are shown in fig. 3 (p. 398).

On this view, at least three isotopes of lithium of mass 6, 7, and 8 are theoretically probable, but even if the combinations were equally stable, the question of their relative abundance in the element lithium on the earth will be dependent on many factors of which we know nothing; for example, the mode of actual formation of such nuclei, the relative amount of the combining units present, and the probability of their combinations.

The experimental results given in the paper support, as far as they go, the view that the atoms of hydrogen and of mass 3 are important units in the nuclear structure of nitrogen and oxygen. In the latter case, one could *a priori* have supposed that oxygen was in some way a combination of four helium nuclei of mass 4. It seems probable that the mass 3 is an important unit of the nuclei of light atoms in general, but it is not unlikely, with increasing complexity of the nuclei and corresponding increase of the electric field, the structures of mass 3 suffer a rearrangement and tend to revert to the presumably more stable nucleus of mass 4. This may be the reason why helium of mass 4 always appears to be expelled from the radio-active atoms, while the isotope of mass 3 arises in the artificial disintegration of lighter atoms like oxygen and nitrogen. It has long been known that for many of the elements the atomic weights can be expressed by the formula $4n$ or $4n+3$, where n is an integer, suggesting that atoms of mass 3 and 4 are important units of the structure of nuclei.*

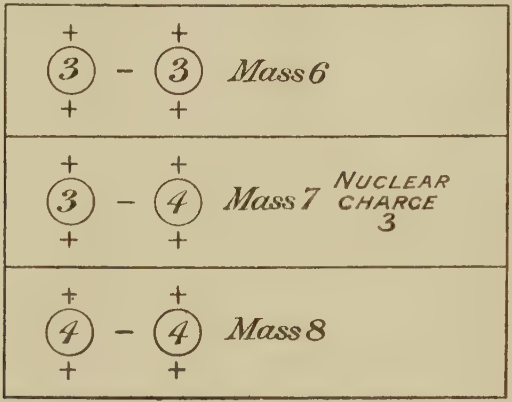

Fig. 3.

Structure of Carbon, Oxygen, and Nitrogen Nuclei.

In the light of the present experiments, it may be of interest to give some idea, however crude, of the possible formation of the above atoms to account for the experimental facts. It will be remembered that nitrogen alone gives rise to H atoms while carbon and oxygen do not. Both nitrogen and oxygen give rise to atoms of mass 3, while carbon has not yet been investigated from this point of view. A possible structure is shown in fig. 4 when the masses and charges of the combining units are indicated. Negative electrons are represented by the symbol —.

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* From these and other considerations, Harkins ('Phys. Rev.,' vol. 15, p. 73 (1920)) has proposed a constitutional formula for all the elements. The combining units employed by him are electrons and atoms of mass 1, 3, and 4 of nuclear charges 1, 1 and 2, respectively. The unit of mass 3 is taken by him to have a nucleus charge of 1 and not 2, and is thus to be regarded as an isotope of hydrogen and not an isotope of helium.

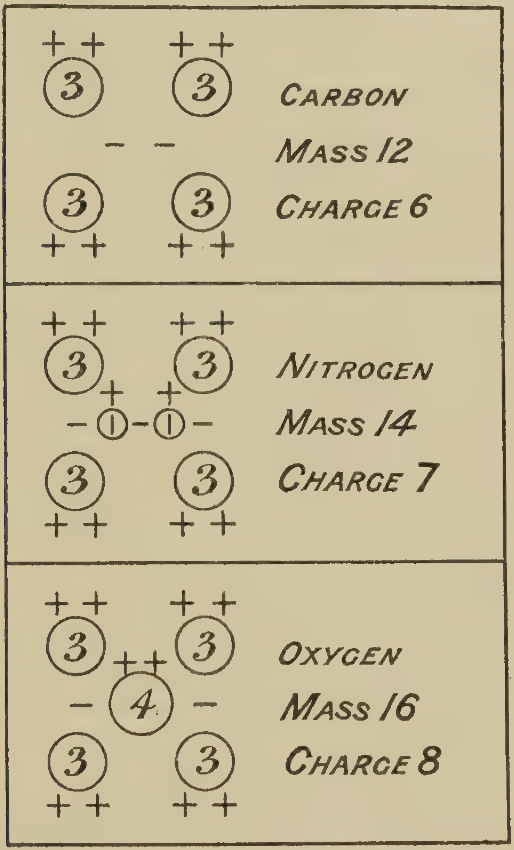

Fig. 4.

The carbon nucleus is taken to consist of four atoms of mass 3 and charge 2, and two binding electrons. The change to nitrogen is represented by the addition of two H atoms with a binding electron and an oxygen nucleus by the substitution of a helium nucleus in place of the two H atoms.

We can see from this type of structure that the chance of a direct collision with one of the four atoms of mass 3 in nitrogen is much greater than the chance of removing an H atom, for it is to be anticipated that the main nucleus would screen the H atom from a direct collision except in restricted regions facing the H atoms. This serves to illustrate why the number of H atoms of mass 3 liberated from nitrogen should be much greater than the number of H atoms released under corresponding conditions. It should be borne in mind that the structures outlined are purely illustrative and no importance is attached to the particular arrangement employed.

It is natural to inquire as to the nature of the residual atoms after the disintegration of oxygen and nitrogen, supposing that they survive the collision and sink into a new stage of temporary or permanent equilibrium.

The expulsion of an H atom carrying one charge from nitrogen should lower the mass by 1 and the nuclear charge by 1. The residual nucleus should thus have a nuclear charge 6 and mass 13, and should be an isotope of carbon. If a negative electron is released at the same time, the residual atom becomes an isotope of nitrogen.

The expulsion of a mass 3 carrying two charges from nitrogen, probably quite independent of the release of the H atom, lowers the nuclear charge by 2 and the mass by 3. The residual atom should thus be an isotope of boron of nuclear charge 5 and mass 11. If an electron escapes as well, there remains an isotope of carbon of mass 11. The expulsion of a mass 3 from oxygen gives rise to a mass 13 of nuclear charge 6, which should be an isotope of carbon. In case of the loss of an electron as well, there remains an isotope of nitrogen of mass 13. The data at present available are quite insufficient to distinguish between these alternatives.

It is intended to continue experiments, to test whether any evidence can be obtained of the disintegration of other light atoms besides nitrogen and oxygen. The problem is more difficult in the case of elements which cannot be conveniently obtained in the gaseous state, since it is not an easy matter to ensure the absence of hydrogen or to prepare uniform thin films of such substances. For these reasons, and the strain involved in counting scintillations under difficult conditions, further progress is not likely to be rapid.

I am indebted to my assistant, G. A. R. Crowe, for the preparation of the radio-active sources and his help in counting; also to Mr. J. Chadwick and Dr. Ishida for assistance in counting scintillations in some of the later experiments.

Symmetrisable Functions and their Expansion in Terms of Biorthogonal Functions.

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(Communicated by Prof. E. W. Hobson, Sc.D., F.R.S. Received April 12, 1920.)

The purpose of this communication is to announce certain results relative to the expansion of a symmetrisable function $\kappa(s, t)$ in terms of a complete biorthogonal system of fundamental functions,* which belong to $\kappa(s, t)$ regarded as the kernel of a linear integral equation. An indication of the method by which the results have been obtained is given, but no attempt is made to supply detailed proofs.

Preliminary Explanations.

§ 1. Let $\kappa(s, t)$† be a function defined in the square $a \leq s \leq b$, $a \leq t \leq b$. If a function $\gamma(s, t)$ can be found which is of positive type in the square $a \leq s \leq b$, $a \leq t \leq b$, and such that

$$\int_a^b \gamma(s, x)\, \kappa(x, t)\, dx$$

is a symmetric function of s and t, $\kappa(s, t)$ is said to be *symmetrisable on the left* by $\gamma(s, t)$ in the square. Similarly, if a function $\gamma'(s, t)$ of positive type can be found such that

$$\int_a^b \kappa(s, x)\, \gamma'(x, t)\, dx$$

is a symmetric function of s and t, $\kappa(s, t)$ is said to be *symmetrisable on the right* by $\gamma'(s, t)$.‡

In general theory the function by which $\kappa(s, t)$ is symmetrisable is usually assumed to be definite.§ The result is that the theory is only applicable to particular forms of the two most important types of symmetrisable function.[*] In order to remove this blemish the notion of a "completely" symmetrisable function has been introduced. Further justification for this departure from the usual practice will be found in the expansion theorems stated below.

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* For the definition of a fundamental function, reference may be made to Goursat, 'Cours d'Analyse,' vol. 3, § 568.

† For brevity, conditions as to summability, etc., are not stated in this section. There will be no difficulty in supplying these conditions.

‡ In what follows, functions symmetrisable on the left will be considered almost exclusively.

§ Lalesco, 'Introduction à la Théorie des Équations Intégrales,' p. 78 (1912); also Goursat, 'Cours d'Analyse,' vol. 3, § 596, pp. 466–8 (1914). Marty ('Comptes Rendus,' t. 150, p. 1031), at first imposed only the condition that the function should be of positive type. He found, however, that this condition was too wide as a basis for a general theory (see footnote, *op. cit*, p. 1500). For the definition of the term "definite," *vide* Goursat, *ov. cit.*, § 5901.

Let $\kappa(s, t)$ be symmetrisable on the left by $\gamma(s, t)$. The function $\kappa(s, t)$ will be said to be *completely symmetrisable on the left* by $\gamma(s, t)$ if either (i) no solution of a homogeneous integral equation of the type

$$\phi(s) = \lambda \int_a^b \kappa(s, t)\, \phi(t)\, dt$$

exists; or (ii) this equation can be solved for one or more values of λ, but no solution is such that $\int_a^b \gamma(s, t)\phi(t)\, dt = 0$. In the first case $\kappa(s, t)$, considered as the kernel of a linear integral equation, has no singular value: in the second case it has at least one singular value.

As an example consider

$$\kappa(s, t) = \alpha(s)\gamma(s, t),$$

where $\gamma(s, t)$ is of positive type in the square $a \leq s \leq b$, $a \leq t \leq b$, and $\alpha(s)$ is a function defined in the interval (a, b). It may be verified that $\kappa(s, t)$ is completely symmetrisable on the left by $\gamma(s, t)$, and is completely symmetrisable on the right by $\alpha(s)\gamma(s, t)\alpha(t)$. This function is associated with the name of Hilbert.[†]

A second example is furnished by

$$\kappa(s, t) = \int_a^b \alpha(s, x)\gamma(x, t)\, dx,$$

where $\gamma(s, t)$ is as before, and $\alpha(s, t)$ is *any* function which is symmetric in the square $a \leq s \leq b$, $a \leq t \leq b$. In this case $\kappa(s, t)$ is completely symmetrisable on the left by $\gamma(s, t)$, and is completely symmetrisable on the right by

$$\int_a^b \int_a^b \alpha(s, x)\gamma(x, y)\alpha(y, t)\, dx\, dy.$$

This type of symmetrisable function was indicated by Marty.[‡]

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[*] These are described at the end of this paragraph.

[†] *Vide* 'Grundzüge einer allgemeinen Theorie der linearen Integralgleichungen, pp. 195–204 (1912). The generalisation $a(s)\gamma(s, t)\beta(t)$ was pointed out by Goursat.

[‡] Comptes Rendus,' t. 150, p. 1500 (1910), footnote.

§ 2. The following properties of a kernel $\kappa(s, t)$ which is completely symmetrisable on the left by $\gamma(s, t)$ can be established*:—

(i) *Either* $\int_a^b \gamma(s, x)\,\kappa(x, t)\,dx = 0$ *or* $\kappa(s, t)$ *has at least one singular value.*

(ii) *A singular value of* $\kappa(s, t)$ *is necessarily real.*

(iii) *A pole of the resolvent*† *is necessarily simple.*

(iv) *Let* $\int_a^b \gamma(sx)\,\kappa(x, t)\,dx \neq 0$, *and let the numbers* $\lambda_1, \lambda_2, \ldots \lambda_n \ldots$ *consist of the singular values of* $\kappa(s, t)$ *each repeated that number of times which corresponds to the order of the singular value considered as a zero of the determinant of* $\kappa(s, t)$. *Then, corresponding to a number* λ_n, *there is a pair of functions* $\phi_n(s)$, $\psi_n(s)$ *which satisfy the homogeneous equations*

$$\phi_n(s) = \lambda_n \int_a^b \kappa(s, t)\,\phi_n(t)\,dt,$$

$$\psi_n(t) = \lambda_n \int_a^b \psi_n(s)\,\kappa(s, t)\,ds,$$

and are such that no linear equation connects functions $\phi_n(s)$ (*or* $\psi_n(s)$) *corresponding to the same singular value. Moreover, the pairs of functions* $\phi_n(s)$, $\psi_n(s)$ *can be chosen in such a way that* (I)

$$\left.\begin{matrix} \phi_1(s), & \phi_2(s), \ldots, & \phi_n(s), & \ldots \\ \psi_1(s), & \psi_2(s), \ldots, & \psi_n(s), & \ldots \end{matrix}\right\} \tag{1}$$

forms a biorthogonal system of functions for the interval (a, b)‡ *and* (II) $\psi_n(s) = \mu_n \int_a^b \gamma(s, t)\,\phi_n(t)\,dt$, *where* μ_n *is a positive constant.*

The functions $\phi_n(s)$ can be so chosen that μ_n is unity, but it appears to be advisable not to do this, in order to preserve symmetry in statements of certain results. In the case of a function completely symmetrisable on both sides there will be a number μ_n', where $\phi_n(s) = \mu_n' \int_a^b \gamma'(s, t)\,\psi_n(t)\,dt$, and it is supposed that the function is symmetrisable on the right by $\gamma'(s, t)$. It is possible to choose the biorthogonal system in such a way that μ_n is always unity, or that μ_n' is always unity. In general, however, it is not possible to secure that μ_n and μ_n' are *both* unity.§

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* The proofs follow closely those given by Lalesco, *op. cit.*, pp. 80–82.

† Reciprocal function, solving function.

‡ It is understood by this that $\int_b^a \phi_n(s)\,\psi_m(s)\,ds = 0$ or 1, according as $n \neq m$ or $n = m$.

§ Lalesco (*op. cit.*, p. 84) appears to have overlooked this fact.

The functions (1) having the properties stated in (iv) will be called a *complete biorthogonal system of fundamental functions* for the kernel $\kappa(s,t)$.

§ 3. The results stated in the preceding paragraph may be regarded as generalisations of the corresponding well-known results for a symmetric function.* It is therefore natural to enquire how far the expansion theorems (*e.g.*, those of Hilbert and Schmidt) connected with the symmetric function can be extended to the more general class. The most important published results in this direction have been obtained by Pell† and Garbe.‡ The first writer develops a theory of biorthogonal systems of functions, and upon this basis establishes an expansion theorem. From the point of view here adopted the most interesting feature of the theorem is its application to the function $\kappa(s,t) = \int_a^b \alpha(s,x)\,\gamma(x,t)\,dx$. It follows, in fact, that when $\kappa(s,t)$ is of this form any function which can be expressed as $\int_a^b \kappa(s,t)\,g(t)\,dt$ admits of an expansion

$$f(s) = \left\{\phi_1(s)\int_a^b f(t)\,\psi_1(t)\,dt + \phi_2(s)\int_a^b f(t)\,\psi_2(t)\,dt + \ldots + \phi_n(s)\int_a^b f(t)\,\psi_n(t)\,dt + \ldots\right\} + h(s),$$

where $h(s)$ is such that $\int_a^b \gamma(s,t)\,h(t)\,dt = 0$, and the series in the brackets is absolutely and uniformly convergent. The function $h(s)$ may be zero, and certainly will be so when $\gamma(s,t)$ is definite.

Garbe§ proves that when $\kappa(s,t) = \alpha(s)\,\gamma(s,t)$ the statements just made are also valid. He then restricts $\gamma(s,t)$ to be "allgemein"‖ and proves that under this condition $\kappa(s,t)$ can be expanded in the form¶

$$\frac{\phi_1(s)\,\psi_1(t)}{\lambda_1} + \frac{\phi_2(s)\,\psi_2(t)}{\lambda_2} + \ldots + \frac{\phi_n(s)\,\psi_n(t)}{\lambda_n} + \ldots.$$

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[*] A symmetric function $\kappa(s,t)$ is completely symmetrisable on either side by the iterated function $\kappa_2(s,t)$.

[†] "Applications of Biorthogonal Systems of Functions to the Theory of Integral Equations," 'Trans. Amer. Math. Soc.,' 1911, p. 173, §4. The condition (c_1), p. 167, and the footnote on p. 165, should be noted in connection with the definition of a completely symmetrisable function given above. In virtue of this condition the theorem lacks generality in its statement.

[‡] 'Mathematische Annalen,' vol. 76, pp. 533–4 (1914–15).

[§] Garbe does not impose any restriction upon $\gamma(s,t)$.

[‖] Hilbert, *op. cit.*, p. 25. The term is somewhat misleading, since "allgemein" kernels are a very restricted class.

[¶] Pp. 538–542, Garbe states the result in a slightly different form.

A result of this kind is suggested by the known expansion of a symmetric function of positive type in terms of its fundamental functions.* It is easy to see, however, that an expansion which contains *only* terms of the form $\phi_n(s)\psi_n(t)/\lambda_n$ is not valid for all symmetrisable functions, not even for the comparatively simple ones of the Hilbert type. In the following paragraph an example is given in justification of this statement. The example will also serve as an existence theorem in connection with the general forms of expansion given below.

§ 4. *Example.*

Let $a = 0$, $b = \pi$; and let $\phi_r(s)$, $\psi_r(s)$, $\xi_r(s)$, $\eta_r(s)$, $(r = 1, 2)$ be functions defined as follows :—

$$\psi_1(s) = \sqrt{1/\pi}\,(1+\cos 3s),$$

$$\psi_2(s) = \sqrt{2/\pi}\,(\cos 7s+\cos 10s),$$

$$\eta_1(s) = \sqrt{2/\pi}\,\cos s,$$

$$\eta_2(s) = \sqrt{2/\pi}\,\cos 5s,$$

$$\phi_n(s) = \alpha(s)\,\psi_n(s)\ (n = 1, 2),$$

$$\xi_n(s) = \alpha(s)\,\eta_n(s)\ (n = 1, 2),$$

where $\alpha(s) = \cos 3s$. Then it may be verified that

$$\left.\begin{matrix} \phi_1(s), & \phi_2(s) \\ \psi_1(s), & \psi_2(s) \end{matrix}\right\}, \tag{2}$$

is a biorthogonal system of functions for the interval $(0, \pi)$; that $\eta_1(s)\,\eta_2(s)$ is an orthogonal system of functions for the same interval;† and that each of the pairs of functions $\{\phi_n(s), \eta_m(s)\}$, $\{\psi_n(s), \xi_m(s)\}$, $\{\xi_n(s), \eta_m(s)\}$ is orthogonal for the interval, whatever be the value of n and m.‡ It will be found that $\xi_1(s)$ and $\xi_2(s)$ are not orthogonal.

Let

$$\gamma(s, t) = \sum_{n=1}^{2} \frac{\psi_n(s)\,\psi_n(t)}{\lambda_n} + \sum_{n=1}^{2} \frac{\eta_n(s)\,\eta_n(t)}{v_n}, \tag{3}$$

and let

$$\kappa(s, t) = \sum_{n=1}^{2} \frac{\phi_n(s)\,\psi_n(t)}{\lambda_n} + \sum_{n=1}^{2} \frac{\xi_n(s)\,\eta_n(t)}{v_n}, \tag{4}$$

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* 'Phil. Trans,' Series A, vol. 209, pp. 439–446.

† It is understood by this that $\int_a^b \eta_n(s)\,\eta_m(s)\,ds = 0$ or 1, according as $n \neq m$ or $n = m$.

‡ *I.e.*, $\int_b^a \phi_n(s)\,\eta_m(s)\,ds = \int_a^b \psi_n(s)\,\xi_m(s)\,ds = \int_a^b \xi_n(s)\,\eta_m(s)\,ds = 0$ for $n = 1, 2$, and $m = 1, 2$.

where λ_1, λ_2, υ_1, υ_2 are any real positive members. It will be clear that $\kappa(s,t) = \alpha(s)\gamma(s,t)$, where $\gamma(s,t)$ is of positive type in the square $0 \leq s \leq \pi$, $0 \leq t \leq \pi$. Inspection of the expression which defines $\kappa(s,t)$ will show that it consists of four kernels, any one of which is orthogonal* to each of the other three. From this it follows that the resolvent corresponding to $\kappa(s,t)$ is

$$K(\lambda;\, s,\, t) = \sum_{n=1}^{2} \frac{\phi_n(s)\,\psi_n(t)}{\lambda_n - \lambda} + \sum_{n=1}^{2} \frac{\xi_n(s)\,\eta_n(t)}{\upsilon_n},$$

and hence that the system (2) is a complete biorthogonal system of fundamental functions for $\kappa(s,t)$. It will now be seen that $\kappa(s,t)$ contains terms $\xi_n(s)\,\eta_n(t)/\upsilon_n$ which are of a character totally different from that of the terms $\phi_n(s)\,\psi_n(t)/\lambda_n$.

§ 5. A more precise account of the results which have been obtained can now be given. In § 7 below it is shown that, if $\kappa(s,t)$ is completely symmetrisable on the left by $\gamma(s,t)$, then $\gamma(s,t)$ admits of an expansion of the form (3). In general the expansion will contain an infinite number of terms of the type $\psi_n(s)\,\psi_n(t)/\mu_n$,† and an infinite number of terms of the type $\eta_n(s)\,\eta_n(t)/\upsilon_n$. When either or both sets of terms is infinite, it is shown that, under very general conditions, the infinite series corresponding to such a set is absolutely and uniformly convergent.

The expansion theorem for $\gamma(s,t)$ is then applied to the particular cases (i) $\kappa(s,t) = \alpha(s)\gamma(s,t)$, (ii) $\kappa(s,t) = \int_a^b \alpha(s,x)\,\gamma(x,t)\,dx$, and it is shown that in each case $\kappa(s,t)$ admits of an expansion of the form (4). As before, the number of terms of each type is, in general, infinite, and the convergence of the series of terms of either type is, under general conditions, absolutely and uniformly convergent.

The Expansion Theorems.

§ 6. Let $\kappa(s,t)$ be a symmetric function which is bounded and summable in the square $a \leq s \leq b$, $a \leq t \leq b$. The function will be said to be of positive type in the square if

$$\int_a^b \int_a^b \kappa(s,\,t)\,f(s)\,f(t)\,ds\,dt \geq 0$$

for each function $f(s)$, which is bounded and summable in the interval $a \leq s \leq b$. With this definition the expansion theorem for functions of positive type as given in 'Philosophical Transactions' Series A, vol. 209, pp. 415–446, may be generalised. The following theorem will be of use hereafter:—

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* Lalesco (*op. cit.*, p. 40) may be consulted.

† μ_n is positive, but is not necessarily a singular value of $\kappa(s,t)$.

Let $\kappa(s, t)$ *be a symmetric function of positive type which is bounded and summable in the square* $a \leq s \leq b$, $a \leq t \leq b$; *and let the function be continuous with respect to s in the interval* (a, b) *for any fixed value of t in the same interval. Let* $\psi_1(s), \psi_2(s), \ldots, \psi_n(s), \ldots$ *be a complete orthogonal system of fundamental functions* for the kernel* $\kappa(s, t)$ *corresponding respectively to singular values* $\lambda_1, \lambda_2, \ldots, \lambda_n, \ldots$ † *Then the series*

$$\sum_{n=1} \frac{\psi_n(s)\psi_n(t)}{\lambda_n}, \tag{5}$$

converges absolutely at every point of the square $a \leq s \leq b$, $a \leq t \leq b$, *and has* $\kappa(s, t)$ *for its sum function.*

Further, if $\kappa(s, s)$ *is a continuous function of s in the interval* (a, b), *the series* (5) *is uniformly convergent in the square* $a \leq s \leq b$, $a \leq t \leq b$, *and* $\kappa(s, t)$, *is continuous throughout the square.*‡

The last part of this theorem is remarkable from the point of view of the theory of functions of real variables. It appears that, if $\kappa(s, t)$ is a symmetric bounded and summable function of positive type such that (i) $\kappa(s, t)$ is continuous with respect to s in (a, b), for any fixed value of t in the interval, and (ii) $\kappa(s, s)$ is a continuous function of s in (a, b), then $\kappa(s, t)$ is a continuous function (of *two* variables) in the square $a \leq s \leq b$, $a \leq t \leq b$.

§ 7. Let $\kappa(s, t)$ be a function (not necessarily symmetrical) defined in the square $a \leq s \leq b, a \leq t \leq b$, which is symmetrisable on the left by $\gamma(s, t)$. It will be assumed that $\kappa(s, t)$ and $\gamma(s, t)$ are each bounded and summable in the square, and that each is a continuous function of s (t)§ in the interval (a, b) for any fixed value of t (s)§ in the interval. It should be observed that under the hypotheses stated, the functions of the complete biorthogonal system (1) § 2 are all continuous in (a, b).

The first step is to obtain an expansion theorem for $\gamma(s, t)$. For this we make use of the generalised Schwarz inequality

$$\int_a^b \int_a^b \gamma(s, t) f(s) f(t)\, ds\, dt \geq \sum_{n=1}^{m} \frac{1}{\mu_n} \left[\int_a^b f(s)\, \psi_n(s)\, ds\right]^2,$$

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* Under the hypotheses stated, the functions are continuous; *cf.* Hobson, 'Proc. Lond. Math. Soc.,' Series 2, vol. 13, p. 308.

† These are not necessarily distinct; *cf.* § 2.

‡ Since establishing this theorem, I have discovered that it may be deduced from a theorem due to Hobson, 'Proc. Lond. Math. Soc.,' Series 2, vol. 14 (Part I), pp. 24–25. The results stated above follow from the fact that the series, $\Sigma\phi_n(s)\,\phi_n(t)/\lambda_n$, is uniformly convergent with respect to s for a fixed t. This being the case, I do not indicate my method of proof here. It is probable that the reader will be able to supply this proof after perusal of § 8.

§ It may be advisable to point out that two statements are here implied—in one the unbracketed letters are to be taken together, and in the other the bracketed letters are to be taken together.

where $f(s)$ may be assumed to be any bounded function summable in (a, b). The inequality may be written in the form

$$\int_a^b \int_a^b \left\{ \gamma(s, t) - \sum_{n=1}^{m} \frac{\psi_n(s)\,\psi_n(t)}{\mu_n} \right\} f(s)\,f(t)\,ds\,dt \geq 0,$$

whence it may be proved that the series

$$\sum_{n=1} \frac{\psi_n(s)\,\psi_n(t)}{\mu_n}, \tag{6}$$

is absolutely convergent in the square $a \quad s \leq b, a \leq t \leq b$.

It can be proved that $\gamma_1(s, t)$, the sum function of the series (6), is bounded and summable in the fundamental square, and that it is continuous with respect to s in the interval (a, b) for any fixed value of t in the interval: hence $\gamma_2(s, t) = \gamma(s, t) - \gamma_1(s, t)$ has the same properties. In virtue of the generalised Schwarz inequality, it will be seen that $\gamma_2(s, t)$ is of positive type. Applying the theorem of § 6 we find that

$$\gamma_2(s, t) = \sum_{n=1} \frac{\eta_n(s)\,\eta_n(t)}{v_n}, \tag{7}$$

where $\eta_1(s), \eta_2(s) \ldots, \eta_n(s), \ldots$ are a complete orthogonal system of fundamental functions for $\gamma_2(s, t)$ corresponding respectively to singular values $v_1, v_2 \ldots v_2 \ldots$, and the series on the right converges absolutely in the fundamental square. It has now been shown that

$$\gamma(s, t) = \sum_{n=1} \frac{\psi_n(s)\,\psi_n(t)}{\mu_n} + \sum_{n=1} \frac{\eta_n(s)\,\eta_n(t)}{v_n}.$$

By application of Dini's theorem* it is easy to establish that where $\gamma(s, s)$ is continuous in (a, b) the two series on the right of the equation just written converge uniformly, and hence that $\gamma_1(s, t)$, $\gamma_2(s, t)$ are both continuous functions in the fundamental square.

Since $\psi_n(s) = \mu_n \int_a^b \gamma_1(s, t)\,\phi_n(t)\,dt$ it will be seen that $\int_a^b \gamma_2(s, t)\,\phi_n(t)\,dt = 0$ for all values of n, and hence that $\int_a^b \gamma_2(s, x)\,\kappa(x, t)\,dx = 0$.† From this it is evident that $\int_a^b \eta_n(s)\,\kappa(s, t)\,ds = 0$, *i.e.*, each of the functions $\eta_1(s), \eta_2(s), \ldots, \eta_n(s), \ldots$ is orthogonal to $\kappa(s, t)$ on the left.

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* *Cf.* 'Phil. Trans.,' A, vol. 209, p. 440.

† Because $\int_a^b \gamma_2(s x)\,\mathrm{K}(\lambda\,;\ x, t)\,dx$, where $\mathrm{K}(\lambda\,;\ s, t)$ is the resolvent, has no finite singularity when considered as a function of λ (*cf.* Marty, 'Comptes Rendus,' vol. 150, pp. 1031–3).

The following theorem can now be stated :—*Let* $\kappa(s, t)$ *be a function which is bounded and summable in the square* $a \leq s \leq b$, $a \leq t \leq b$; *and let the function be continuous with respect to* s (t) *in the interval* (a, b) *for any fixed value of* t (s) *in this interval. Let* $\kappa(s, t)$ *be completely symmetrisable on the left by a function* $\gamma(s, t)$ *of positive type which has the properties of boundedness, summability, and continuity postulated for* $\kappa(s, t)$. *Finally, let*

$$\phi_1(s), \phi_2(s), \ldots, \phi_n(s), \ldots,$$
$$\psi_1(s), \psi_2(s), \ldots, \psi_n(s), \ldots,$$

be a complete biorthogonal system of fundamental functions for the kernel $\kappa(s, t)$. *Then*

$$\gamma(s, t) = \sum_{n=1} \frac{\psi_n(s)\,\psi_n(t)}{\mu_n} + \sum_{n=1} \frac{\eta_n(s)\,\eta_n(t)}{v_n}, \tag{8}$$

where (i) *the functions* $\eta_n(s)$ $(n = 1, 2, \ldots)$ *are all continuous in the interval* (a, b), *and form an orthogonal system of functions for this interval,* (ii) *each function* $\eta_n(s)$ *is orthogonal to* $\kappa(s, t)$ *on the left,* (iii) *the numbers* μ_n $(n=1, 2, \ldots)$ *are positive and are defined by the equations*

$$\mu_n \int_a^b \int_a^b \gamma(s, t)\, \phi_n(s)\, \phi_n(t)\, ds\, dt = 1;$$

and (iv) *the numbers* v_n $(n = 1, 2, \ldots)$ *are positive. Each of the series on the right of* (8) *is absolutely convergent in the square* $a \leq s \leq b$, $a \leq t \leq b$, *and each has a sum-function which has the properties of boundedness, summability, and continuity postulated for the functions* $\kappa(s, t)$, $\gamma(s, t)$.

Further, if $\gamma(s, s)$ *is a continuous function of* s *in the interval* (a, b), *each of the series on the right of* (8) *is uniformly convergent in the square* $a \leq s \leq b$, $a \leq t \leq b$.

The corresponding result when $\kappa(s, t)$ is completely symmetrisable on the right by $\gamma'(s, t)$ will be obvious. The expansion for $\gamma'(s, t)$ is

$$\sum_{n=1} \frac{\phi_n(s)\,\phi_n(t)}{\mu_n'} + \sum_{n=1} \frac{\xi_n'(s)\,\xi_n'(t)}{v_n'},$$

where the functions $\xi_n'(s)$ $(n = 1, 2 \ldots)$ form an orthogonal system of functions for the interval (a, b), and each function is orthogonal to $\kappa(s, t)$ on the right.

In passing it should be observed that for the function symmetrisable on the left we have

$$\int_a^b \gamma(s, x)\, \kappa(x, t) = \int_a^b \gamma_1(s, x)\, \kappa(x, t) = \sum_{n=1} \frac{\psi_n(s)\,\psi_n(t)}{\lambda_n \mu_n},$$

and that there is a corresponding result for the case of a function symmetrisable on the right.

§ 8. From considerations of lucidity and brevity the theorems of the two preceding paragraphs have not been stated in a form which is sufficiently general in certain applications. Thus Hilbert has shown the function $\alpha(s)\gamma(st)$ to be of interest, where $\alpha(s)$ is a discontinuous function defined by $\alpha(s) = +1$ in certain sub-intervals of (a, b), and $\alpha(s) = -1$ in the complementary intervals.* To meet this and other cases an easy generalisation may be made.

Let $a_1, a_2, \ldots a_{N-1}$ be numbers which satisfy the inequalities $a < a_1 < a_2 \ldots < a_{N-1} < b$, and let a, b be denoted by a_0, a_N respectively. Let $\kappa(s, t)$ be a function which is bounded and summable in the square $a \leq s \leq b, a \leq t \leq b$: let $\kappa(s, t) = \kappa^{(p, q)}(s, t)$ $(p = 1, 2, \ldots N;\ q = 1, 2, \ldots, N)$ in the *open* rectangle $a_{p-1} < s < a_p$, $a_{q-1} < t < a_q$, where $\kappa^{(p, q)}(s, t)$ is defined in the *closed* rectangle $a_{p-1} \leq s \leq a_p$, $a_{q-1} \leq t \leq a_q$, and is (i) continuous with respect to s in the closed interval (a_{p-1}, a_p) for any fixed value of t in the closed interval (a_{q-1}, a_q); (ii) continuous with respect to t in the closed interval (a_{q-1}, a_q) for any fixed value of s in the closed interval (a_{p-1}, a_p). Let $\gamma(s, t)$ be a function of positive type which has properties similar to those postulated for $\kappa(s, t)$, and let $\kappa(s, t)$ be symmetrisable on the left by $\gamma(s, t)$. It is easily proved that, in the open interval $a_{p-1} < s < a_p$, $\phi_n(s)$ is equal to a function $\phi_n^{(p)}(s)$, which is continuous in the closed interval $a_{p-1} \leq s \leq a_p$; and similarly in regard to $\psi_n(s)$, $\eta_n(s)$. Thus, corresponding to a rectangle $a_{p-1} \leq s \leq a_p$, $a_{q-1} \leq t \leq a_q$, we have continuous functions $\kappa^{(p, q)}(s, t)$, $\gamma^{(p, q)}(s, t)$, $\phi_n^{(p)}(s)$, $\phi_n^{(q)}(t)$, $\psi_n^{(p)}(s)$, $\psi_n^{(q)}(t)$, $\eta_n^{(p)}(s)$, $\eta_n^{(q)}(t)$ $(n = 1, 2, \ldots)$: these functions will be said to be *associated with* the rectangle.

It will be found that (8) is valid under the conditions just stated provided that, when the point (s, t) is on the boundary of a rectangle such as is described above, each of the various functions occurring in the equations is understood to mean the corresponding function ($\gamma^{(p, q)}(s, t)$, $\psi_n^{(p)}(s)$, etc.) associated with any one rectangle to which (s, t) may be regarded as belonging. Thus the point (a_1, a_1) may be regarded as belonging to four rectangles, and hence (8) is (for $s = a_1$, $t = a_1$) equivalent to

$$\gamma^{(p, q)}(a_1, a_1) = \sum_{n=1} \frac{\psi_n^{(p)}(a_1)\,\psi_n^{(q)}(a_1)}{\mu_n} + \sum_{n=1} \frac{\eta_n^{(p)}(a_1)\,\eta_n^{(q)}(a_1)}{\nu_n}$$

for $p = 1, 2$ and $q = 1, 2$. It will be understood that two or more of the equations just written may be identical, owing to the fact that corresponding functions associated with different rectangles have the same values for $s = a_1$, $t = a_1$.

Each of the series on the right of (8) is absolutely convergent in the square

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* Hilbert, *op. cit.*, Chap. 16, may be consulted.

$a \leq s \leq b$, $a \leq t \leq b$, and, further, each is uniformly convergent in the square when $\gamma^{(p,p)}(s, s)$ is continuous in the interval $a_{p-1} \leq s \leq a_p$ for $p = 1, 2, \ldots, N$.

§ 9. Let us now consider Hilbert's function

$$\kappa(s, t) = \alpha(s)\gamma(s, t)\ (a \leq s \leq b,\ a \leq t \leq b),$$

where $\alpha(s)$ is bounded in (a, b) and is continuous at all except a finite number of points of the interval, and $\gamma(s, t)$ is a function of positive type which has the properties specified in § 7.* Since $\kappa(s, t)$ is symmetrisable on the left by $\gamma(s, t)$, it follows from the theorem of § 7 that

$$\gamma(s, t) = \sum_{n=1} \frac{\psi_n(s)\psi_n(t)}{\mu_n} + \sum_{n=1} \frac{\eta_n(s)\eta_n(t)}{v_n}.$$

Multiplying through by $\alpha(s)$, it will be found that

$$\kappa(s, t) = \sum_{n=1} \frac{\phi_n(s)\psi_n(t)}{\lambda_n} + \sum_{n=1} \frac{\xi_n(s)\eta_n(t)}{v_n}, \tag{9}$$

where $\xi_n(s) = \alpha(s)\eta_n(s)$ and, of course, $\eta_n(s)$ $(n = 1, 2, \ldots)$ constitute an orthogonal system of functions for the interval (a, b), each member of which is orthogonal to $\kappa(s, t)$ on the left.† If we now multiply through the equation (9) by $\eta_m(s)$, and integrate between the limits a and b, we find

$$0 = \sum_{n=1} \frac{\eta_n(t)\int_a^b \xi_n(s)\eta_m(s)\,ds}{v_n},$$

whence it appears that $\int_a^b \xi_n(s)\eta_m(s)\,ds = 0$ for all values of n and m. Thus $\kappa(s, t)$ *can be expressed in the form* (9), *where* (i) *the functions* $\eta_n(s)$ $(n = 1, 2, \ldots)$ *constitute an orthogonal system of functions for the interval* (a, b), *and* (ii) *each of the pairs of functions* $\{\xi_n(s), \psi_m(s)\}$, $\{\eta_n(s), \phi_m(s)\}$, $\{\xi_n(s), \eta_m(s)\}$ *is orthogonal for the interval* (a, b) *whatever be the values of* n *and* m.‡

Let it be assumed that $\alpha(s)$ has only one sign in the interval (a, b).§ Since

$$\int_a^b \alpha(s)[\eta_n(s)]^2\,ds = \int_a^b \xi_n(s)\eta_n(s)\,ds = 0$$

it will be clear that $\xi_n(s)$ cannot exist.

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* The results obtained are valid when $\gamma(s, t)$ is subject to the wider conditions of § 8.

† The singular values λ_n are not subject to any restriction as to sign: there may be an infinite number of positive singular values and an infinite number of negative singular values.

‡ These are referred to as the orthogonal properties of the functions $\phi_n(s)$, $\psi_n(s)$, $\xi_n(s)$, $\eta_n(s)$, in the next paragraph.

§ $a(s)$ may be zero at points in the interval.

Again, let it be assumed that $\gamma(s, t)$ is definite. It follows from the relation

$$\int_a^b \eta_n(s)\,\kappa(s, t)\,ds = 0,$$

that

$$\int_a^b \xi_n(s)\,\gamma(s, t)\,ds = 0,$$

and hence that $\xi_n(s)$ cannot exist.

It is thus seen that when $\alpha(s)$ has only one sign in $(a\ b)$, or when $\gamma(s, t)$ is definite,

$$\kappa(s, t) = \sum_{n=1} \frac{\phi_n(s)\,\psi_n(t)}{\lambda_n}. \tag{10}$$

It will be clear that the series on the right of (9) are each uniformly convergent in the fundamental square, when $\gamma(s, s)$ is continuous in the interval (a, b).

§ 10. Consider next the function

$$\kappa(s, t) = \int_a^b \alpha(s, x)\,\gamma(x, t)\,dx,$$

where $\alpha(s, t)$ is a symmetric function (not necessarily of positive type) and $\gamma(s, t)$ is a symmetric function of positive type in the square $a \leq s \leq b$, $a \leq t \leq b$. It will be assumed that each of the functions $\alpha(s, t)$ $\gamma(s, t)$ is bounded and summable in the square $a \leq s \leq b$, $a \leq t \leq b$, and that each is continuous with respect to s in the interval (a, b) for any fixed value of t in the interval.* Proceeding as in § 9, it will be found that, because $\kappa(s, t)$ is symmetrisable on the left by $\gamma(s, t)$, *we have the equation* (9), *where now* $\xi_n(s) = \int_a^b \alpha(s, t)\,\eta_n(t)\,dt$, *but the orthogonal properties of the functions* $\phi_n(s)$, $\psi_n(s)$, $\xi_n(s)$, $\eta_n(s)$ *are exactly as before.*

It can be shown that, if $\alpha(s, t)$ is of positive type, or if $\gamma(s, t)$ is definite, the expansion (10) is valid.

The concluding remark at the end of § 9 applies to this case also.

§ 11. The results indicated in the last two paragraphs have important consequences in the theory of the linear integral equation.

For example, when $\kappa(s, t)$ is of either of the two kinds specified, its resolvent is given by

$$\mathrm{K}(\lambda\,;\, s, t) = \sum_{n=1} \frac{\phi_n(s)\,\psi_n(t)}{\lambda_n - \lambda} + \sum_{n=1} \frac{\xi_n(s)\,\eta_n(t)}{v_n}.$$

In connection with this, it should be observed that the resolvent is symmetrisable on the left by $\gamma(s, t)$.

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* Wider conditions, *e.g.*, on the lines of § 8, may be imposed.

Again, the Fredholm determinant is

$$D(\lambda) = \prod_{n=1} \left(1-\frac{\lambda}{\lambda_n}\right),$$

and is consequently of class ("genre") zero.

Lastly, it may be observed that

$$\sum_{n=1} \frac{1}{\lambda_n} = \int_a^b \kappa(s, s)\, ds.$$

The equation just written leads to interesting results, as to the relation between the singular values of $\kappa(s, t)$ and those of $\gamma(s, t)$.

On the Conditions at the Boundary of a Fluid in Turbulent Motion.

By T. E. Stanton, F.R.S., Miss Dorothy Marshall, B.Sc., and Mrs. C. N. Bryant.

(Communicated from the National Physical Laboratory. Received April 13, 1920.)

The experiments here described form part of a general research into the phenomena of skin friction of solid surfaces due to the flow over them of fluids whose motion, not in the immediate vicinity of the surface, is eddying or turbulent. Considerable information has been obtained in recent years as to the magnitude of the frictional forces brought into existence in this condition of flow, and the manner of variation of these forces with the relative mean speed of surface and fluid, the roughness of the surface, and the physical characteristics of the fluid is fairly well known. Practically nothing, however, is known about the mechanism by which the resistance to flow is transmitted to the bounding surfaces. For speeds below the critical when the general motion of the fluid throughout is streamline in character, it is generally accepted that the layer of fluid in contact with the boundary is at rest relative to it, as any slipping of finite amount would be detected in a variation from the Poiseuille law of the relationship between the diameter of a pipe and the time of efflux of a given volume of fluid. At speeds above the critical, observations near the walls have shown that the mean velocity falls rapidly as the solid bounding surface is approached, and it has been suggested that at the walls there may exist a thin layer in which the flow is laminar in character, in which case, if there is no slipping, the frictional resistance would be determined from the slope of the velocity curve in the surface layer and the coefficient of viscosity of the fluid.

During the last few years several attempts have been made at the National Physical Laboratory to obtain evidence as to the truth of this assumption. The method adopted has been to set up a condition of turbulent fluid motion over a surface of which the frictional resistance to the flow could be accurately determined, and to measure by means of a very fine Pitot tube the velocity of the fluid at a point as near the wall as possible.

The chief difficulties in the method are: (1) the interference in the flow in the neighbourhood of the boundary due to the presence of the tube itself; and (2) the fact that when such a tube was placed in a current of fluid in which the variation of velocity across the mouth of the tube was very great, it is by no means certain that the value of the speed deduced from the pressure in the Pitot tube would be the speed at the geometrical centre of the tube.

From the results of experiments made in 1911* on the distribution of the axial velocity of air flowing in pipes of 4·9 cm. and 7·4 cm. diameter, it appeared that the thickness of the layer of fluid which was in a state of laminar motion at the walls, if it existed at all, was certainly less than half a millimetre; and when, by the appointment in 1916 of Miss C. N. Jones (Mrs. Bryant) as a research worker in fluid motion, an opportunity occurred of taking the matter up again, attempts were made to produce a Pitot tube sufficiently small to explore the region of these dimensions. The smallest tube which could be used satisfactorily was one of which the external dimensions at the orifice were $0·1 \times 0·8$ mm. and the internal dimensions $0·05 \times 0·75$ mm.

The first set of observations was directed to an estimation of the reliability of the instrument as an indicator of the square of the speed at the geometrical centre of the orifice of the Pitot tube, when this was placed close to the wall of the pipe. For this purpose, the speed of the flow in the pipe (0·714 cm. diameter) was kept below its critical value (580 cm. per second), so that the distribution of velocity across any section could be calculated from the formula $V = V_c(1-r^2/a^2)$, where V_c is the velocity at the axis of the pipe and a is the radius of the pipe.

A satisfactory check between observed speeds and theoretical speeds was obtained up to a distance of 0·25 mm. from the walls. It has been inferred by Morrow from observations on the distribution of velocity of water flowing through a pipe at speeds below the critical, that this theoretical

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* 'Roy. Soc. Proc.,' A, vol. 85, p. 366.

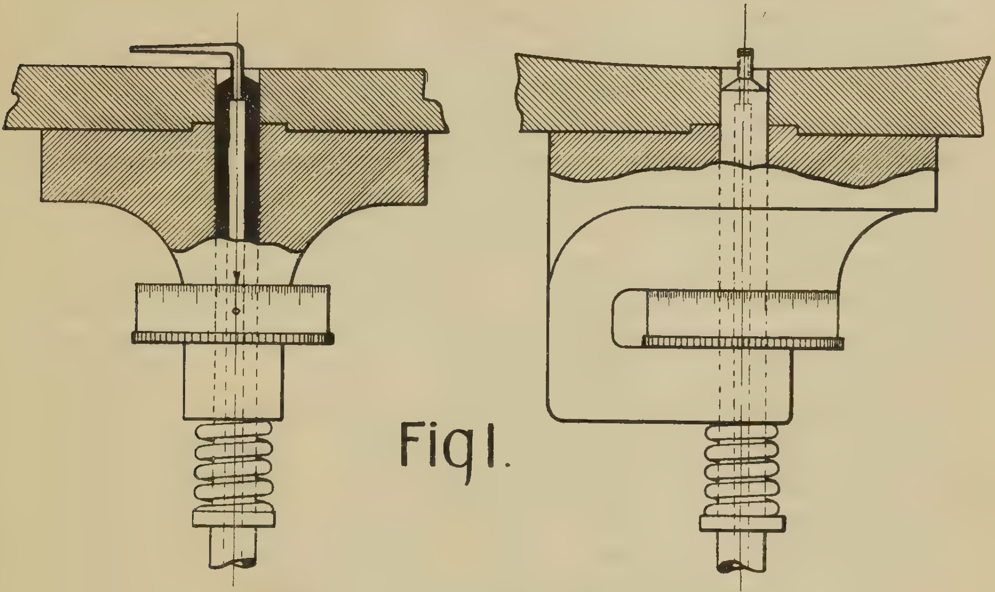

Fig 1.

Pitot Tube N° 1 Scale 2/1

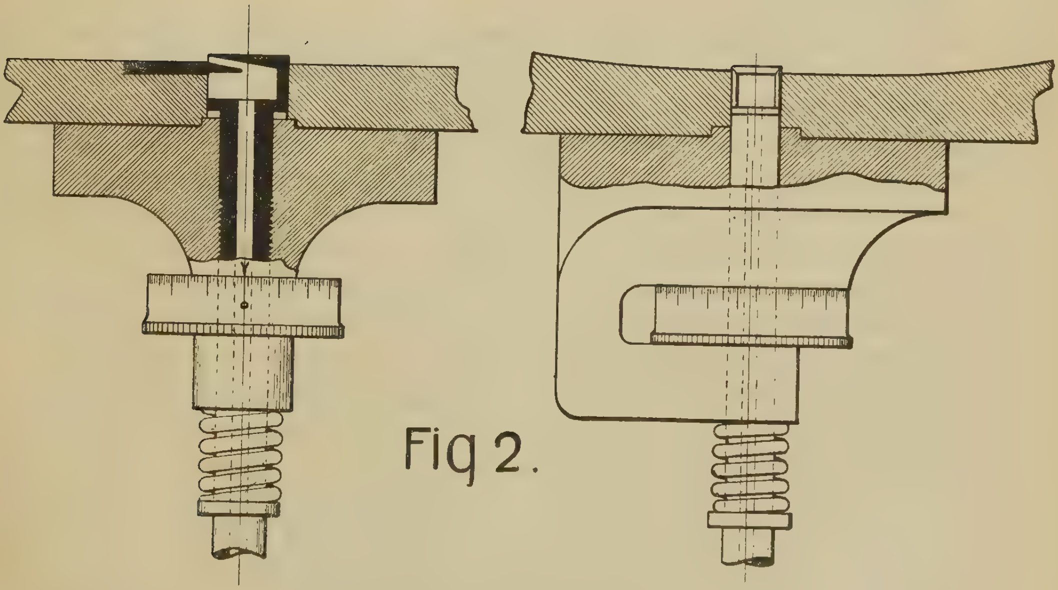

Fig 2.

Pitot Tube N° 2 Scale 2/1

distribution is not that which actually exists.* This deduction, however appears to be due partly to a small inaccuracy in the calibration of the Pitot tube used and partly to the fact that in Morrow's experiments the Pitot tube was situated at a section of the tube which was approximately 30 diameters from the inlet end of the tube. It is almost certain that at this distance the radial distribution of velocity has not reached steady conditions. No appreciable departure from the parabolic distribution of flow has been found in the National Physical Laboratory experiments at distances of 100 diameters from the inlet. At distances closer to the walls than 0·25 mm. the sensitiveness of the manometer employed was not sufficient to measure the differences between the Pitot and static pressures with sufficient accuracy for the purpose of making the desired comparison.

The difficulty of measuring the velocity at distances from the walls of less than 0·25 mm. will be realised from the fact that, with a velocity at the axis of 1050 cm. per second, the velocity at a distance of 0·1 mm. from the wall is only 58 cm. per second, corresponding with a pressure head on the manometer of 0·02 mm. of water. As the readings of the very sensitive manometer employed for the work could not be depended upon to an accuracy greater than +0·005 mm. of water, it is obvious that no reliable comparison between the actual and theoretical speeds at this distance from the wall could be obtained.

In the second series of experiments, observations of the pressure differences between the Pitot and static pressure tubes, for a given distance of the geometrical centre of the former from the walls, were taken over as wide a range in the mean rate of flow through the pipe as possible. At the same time, the corresponding slopes of the static pressure gradient down the pipe were accurately determined. From the latter measurements the values of the surface friction at the walls for different rates of flow were calculated. The Pitot tube observations were then repeated for other distances of the tube from the walls (Table I). For each distance a curve of speed variation with surface friction was plotted, and from these curves it was possible to scale off, for any given value of the surface friction, the speeds corresponding to the different distances of the Pitot tube from the walls and so plot a curve showing the variation of speed with position of Pitot tube. These curves are shown in fig. 3. It will be realised, of course, that these curves can only be taken as showing the radial distribution of velocity in the neighbourhood of the walls, under the assumption that the speed indicated by the Pitot tube is that which exists at the geometrical centre of the orifice, *i.e.*, that there is no interference with the flow near the walls due to the presence of the tube. In

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* 'Roy. Soc. Proc.,' A, vol. 76, p. 205.

Table I.—Diameter of Pipe = 0·714 cm.

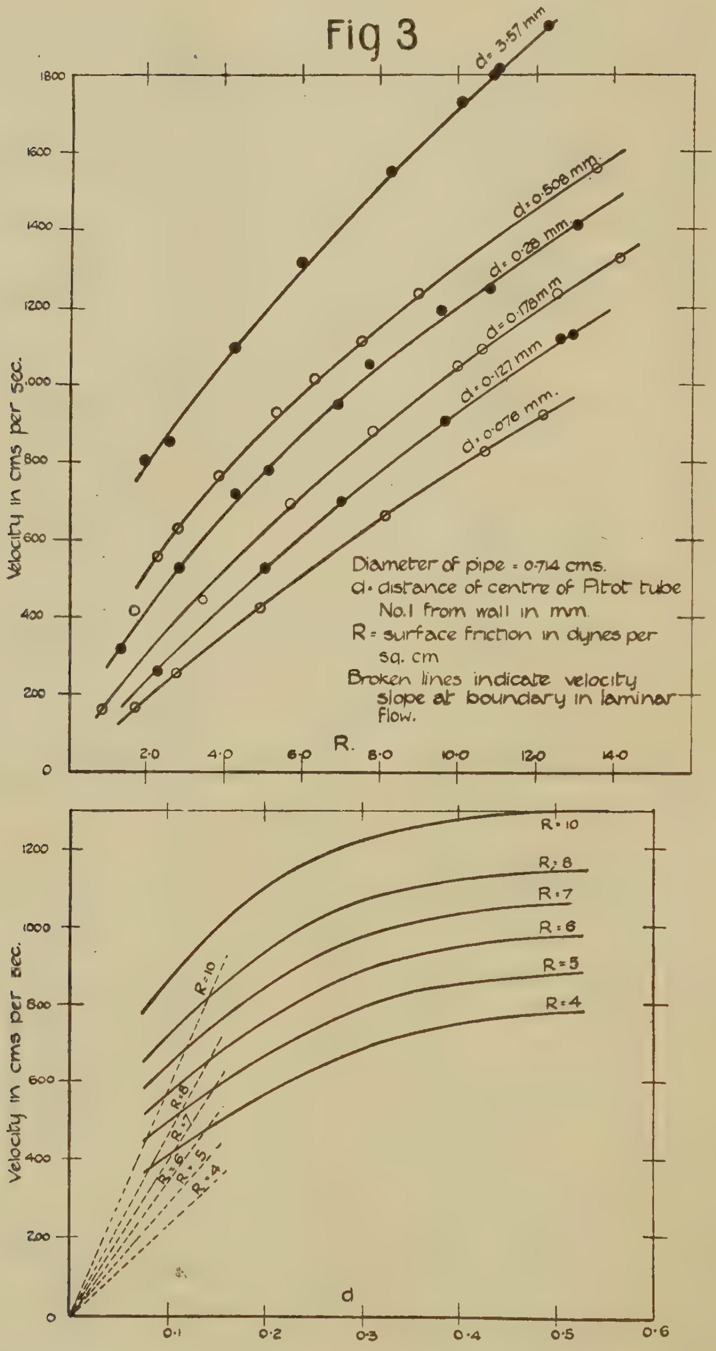
d = 3·568 mm.		d = 0·508 mm.		d = 0·279 mm.		d = 0·179 mm.		d = 0·127 mm.		d = 0·076 mm.	
v. cm. per sec.	R. dynes per sq. cm.	v. cm. per sec.	R. dynes per sq. cm.	v. cm. per sec.	R. dynes per sq. cm.	v. cm. per sec.	R. dynes per sq. cm.	v. cm. per sec.	R. dynes per sq. cm.	v. cm. per sec.	R. dynes per sq. cm.
805	2·00	420	1·68	315	1·35	160	0·84	160	1·22	170	1·68
855	2·60	555	2·29	525	2·87	445	3·46	255	2·27	260	2·72
1095	4·28	630	2·80	720	4·31	690	5·70	525	5·03	425	4·90
1315	6·00	765	3·89	780	5·13	880	7·82	695	7·01	660	8·11
1550	8·27	925	5·34	950	6·96	1050	10·00	905	9·66	830	10·7
1730	10·08	1015	6·31	1050	7·75	1090	10·7	1120	12·6	920	12·2
1800	10·90	1110	7·53	1190	9·56	1230	12·6	1125	12·95		
1817	11·04	1235	9·00	1250	10·8	1325	14·1				
1920	12·29	1560	13·6	1410	13·0						

Table II.—No. 1 Pitot in 12·7 cm. Pipe.

d = 0·267 mm.		d = 0·216 mm.		d = 0·165 mm.		d = 0·114 mm.		d = 0·076 mm.		d = 0·051 mm.	
v. cm. per sec.	R. dynes per sq. cm.	v. cm. per sec.	R. dynes per sq. cm.	v. cm. per sec.	R. dynes per sq. cm.	v. cm. per sec.	R. dynes per sq. cm.	v. cm. per sec.	R. dynes per sq. cm.	v. cm. per sec.	R. dynes per sq. cm.
530	3·80	500	4·26	420	4·07	340	4·00	260	3·1	300	4·9
925	7·9	845	7·9	710	7·9	465	6·2	455	6·9	405	6·7
1090	9·9	990	9·8	830	9·6	600	8·05	600	10·6	480	9·0
1300	12·8	1185	12·7	1045	12·5	700	10·1	815	16·0	585	11·9
1525	16·5	1435	16·7	1285	16·8	705	10·2	1065	23·8	705	16·1
1690	19·8	1620	20·2	1495	20·8	820	12·8	1275	30·1	810	19·5
1890	23·6	1795	23·7	1645	23·8	1030	16·4	—	—	935	23·8
						1150	18·8	—	—	1095	29·9
						1320	22·8				

d = distance of centre of Pitot from wall. v = surface speed. R = friction.

Fig 3


d = 3·57 mm
d = 0·508 mm
d = 0·28 mm
d = 0·178 mm
d = 0·127 mm
d = 0·076 mm
Velocity in cms per sec.
1800
1600
1400
1200
1,000
800
600
400
200
0
2·0
4·0
6·0
8·0
10·0
12·0
14·0
R.
Diameter of pipe = 0·714 cms.
d = distance of centre of Pitot tube No. 1 from wall in mm.
R = surface friction in dynes per sq. cm
Broken lines indicate velocity slope at boundary in laminar flow.
R = 10
R = 8
R = 7
R = 6
R = 5
R = 4
Velocity in cms per sec.
1200
1000
800
600
400
200
0
0·1
0·2
0·3
0·4
0·5
0·6
d

the same figure are shown in dotted lines velocity slopes which would exist at the boundary if the flow were laminar. These are calculated from the known frictional resistances and the value of the coefficient of viscosity for air. Another interesting feature of the velocity distribution is the manner in which the speed at any given distance from the walls varies with the frictional resistance. If the flow were laminar, the velocity at any point would, of course, be simply proportional to the surface friction. For turbulent flow it is known that the surface friction is proportional to the *n*th power of the mean rate of flow, where *n* varies from 1·75 to 2, according to the diameter and roughness of the pipe.

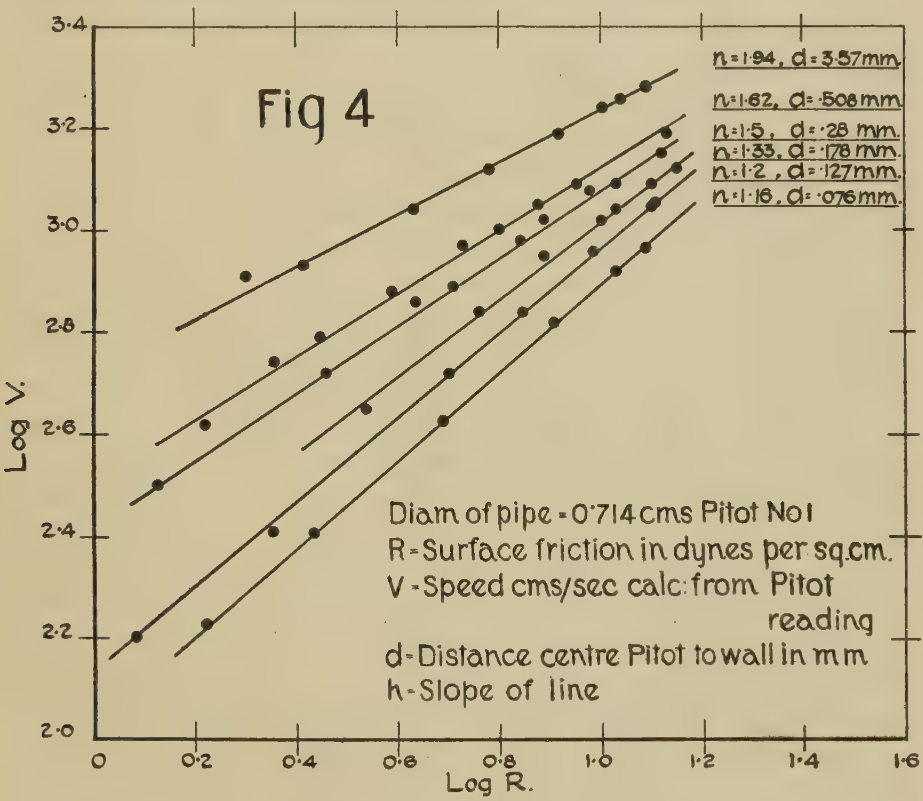


Fig 4

Diam of pipe = 0·714 cms Pitot No 1
R = Surface friction in dynes per sq.cm.
V = Speed cms/sec calc: from Pitot reading
d = Distance centre Pitot to wall in mm
h = Slope of line

This relation is usually obtained by plotting points of which the ordinates and abscissæ are the logarithms of the surface friction and mean flow. These points are found to be on a straight line of which the slope gives the value of *n*. Adopting the same method for velocities at a point, the curves shown on fig. 4 have been obtained. These show that the relation between surface friction and speed at a point near the wall is of the same form as that between surface friction and mean flow, but that the value of n diminishes as the boundary is approached until, when the geometrical centre of the tube is 0·075 mm. from the wall, the value of n is 1·16. It would appear, therefore, that at this distance the eddy motion has nearly disappeared.

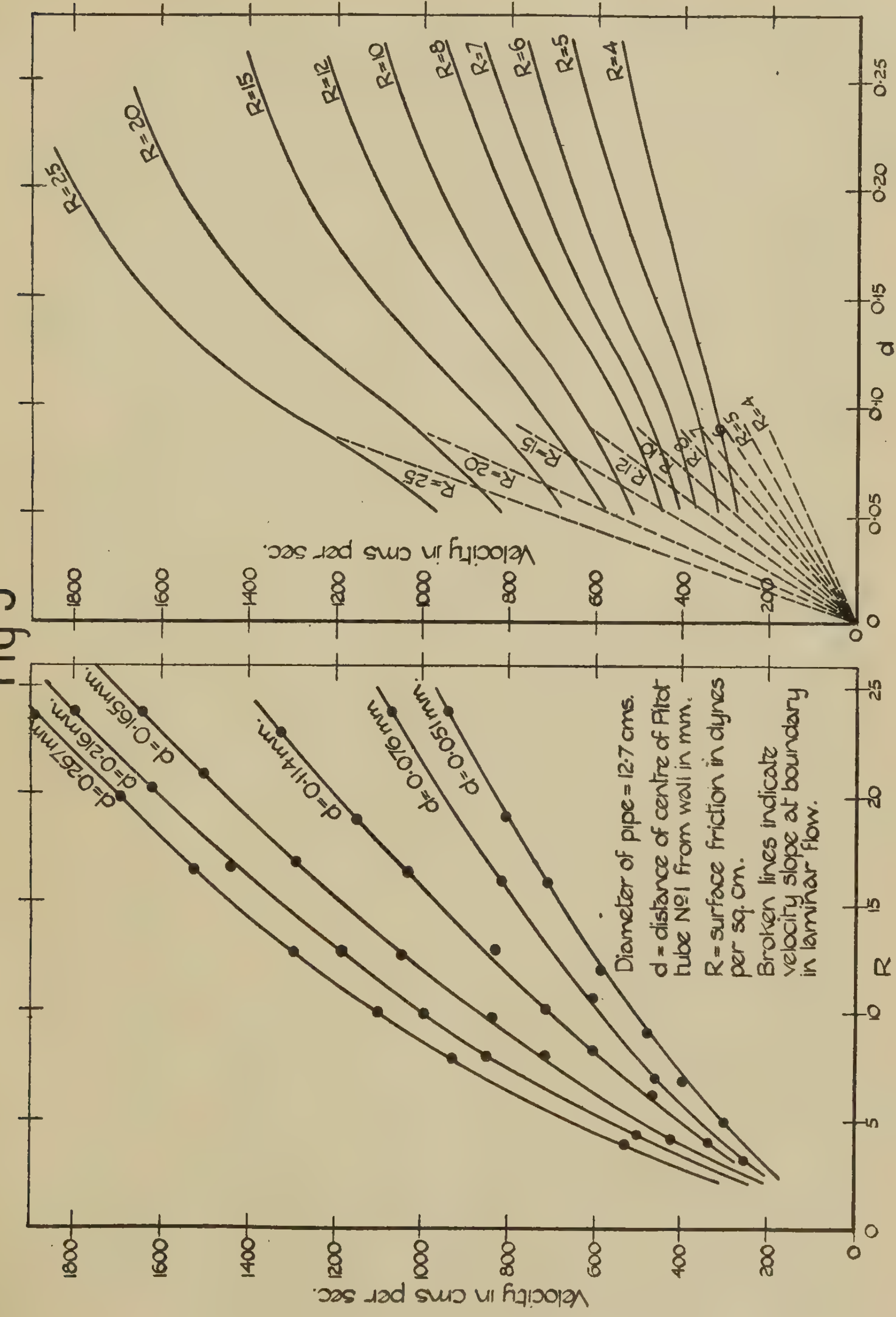
As the experiments in this small pipe (0·714 cm. diameter) were made at speeds not greatly exceeding the critical speed, *i.e.*, at values of $\mathrm{V}.d/\nu$ between 2000 and 5000 (where ν = the kinematic viscosity of air, V = mean rate of flow, and d = diameter of pipe), it was considered desirable to repeat the experiments at values of $\mathrm{V}.d/\nu$ very much greater than this, for it is known that the distribution of the velocity across a pipe changes appreciably with the value of this function.

For this purpose a pipe of 12·7 cm. diameter was used. Air was supplied to this by means of a high-speed Sturtevant fan which could maintain a constant rate of flow through the pipe of about 2900 cm. per second, corresponding with a value of $\mathrm{V}.d/\nu$ of 250,000. The same Pitot tube was used as in the small pipe, the method of attachment being shown in fig. 1. Experiments similar to those described above were made by Miss Marshall, who took up the work after the transfer of Miss C. N. Jones to another division of the laboratory. The observations (Table II) were reduced in the same way as before, and the curves of variation of indicated speed with mean rate of flow and with position of Pitot tube are shown in fig. 5. On examining the curves in figs. 3 and 5, and assuming the interference effects to be negligible, the following characteristics will be seen to be common to both:—

(1) The slopes of the tangents to the velocity curves at distances of 0·075 mm. and above from the walls are very much smaller than would be the case if the flow were laminar at these distances from the wall. For example, when the surface friction in the 0·714 cm. pipe is 10 dynes per square centimetre, the value of $d\mathrm{V}/dr$ at 0·075 mm. from the wall would be 57,200 if the flow were streamline in character. The measured value of $d\mathrm{V}/dr$ was 33,600. In the case of the 5-inch pipe, the corresponding values are 211,200 for streamline motion and 90,000 actually observed.

(2) The speeds calculated from the observations at distances of 0·075 mm. and less from the walls are appreciably higher than would exist in laminar flow with the measured surface friction. For example, in the 0·714 cm. pipe, with a frictional resistance of 10 dynes per square centimetre, the calculated speed at 0·075 mm. from the walls was 795 cm. per second. In laminar flow with this value of the surface friction the speed would be 443 cm. per second. In the case of the 5-inch pipe at a value of the surface friction of 36·1 dynes per square centimetre, and at a distance of 0·5 mm. from the

Fig 5


Velocity in cms per sec.
0
200
400
600
800
1000
1200
1400
1600
1800
d
0·05
0·10
0·15
0·20
0·25
R=25
R=20
R=15
R=12
R=10
R=8
R=7
R=6
R=5
R=4
Velocity in cms per sec.
R
0
5
10
15
20
25
d=0·267mm.
d=0·216mm.
d=0·165mm.
d=0·114mm.
d=0·076mm.
d=0·051mm.
Diameter of pipe = 12·7 cms.
d = distance of centre of Pitot tube No 1 from wall in mm.
R = surface friction in dynes per sq. cm.
Broken lines indicate velocity slope at boundary in laminar flow.

wall, the corresponding values are 1230 for the calculated speed and 1050 for the speed in streamline flow.

To sum up the evidence afforded by the curves of figs. 3 and 5, it would appear that if it may be assumed that the speed indicated by the Pitot tube is the speed of the fluid at its geometrical centre during the experiment, streamline motion if it exists must be confined to a region of less than 0·05 mm. from the boundary, and further, the observations are not inconsistent with a finite amount of slip at the boundary.

It was evident, therefore, that the proof of the existence or otherwise of streamline motion at the boundary would involve a closer exploration of the region near the boundary than had hitherto been possible. This, however, could not be done with the available appliances owing to the fact that any further reduction in the cross dimensions of the Pitot tube would have rendered it unworkable owing to the time fluctuations of pressure in the room. After some consideration it was thought that if the wall of the Pitot tube adjacent to the wall of the pipe could be removed and its place taken by the wall of the pipe itself, it would be possible to obtain readings at distances of 0·025 and 0·01 mm. from the wall. The arrangement of tube previously used was accordingly modified and the final form adopted is shown in fig. 2. This was set up in the 5-inch pipe and a series of observations (Table III) similar to those previously described were made and reduced in the same way as before. The final results are shown in the curves of fig. 6 which give the variation of the velocity calculated from the new Pitot tube pressures with the surface friction and with the distance of the geometrical centre of the tube opening from the wall of the pipe.

From an examination of these curves it will be seen that by means of the new device the nature of the flow in the region of the boundary is revealed to a very much greater extent than was possible with the original form of Pitot tube, and that the new evidence afforded by the velocity estimations up to within 0·01 mm. from the wall strengthens considerably the probability of the existence at the boundary of a layer of fluid of finite thickness which is in streamline motion. The existence of a slip at the boundary is not, however, decidedly negatived, as it will be seen from fig. 6 that the values of the speeds at 0·01 mm. from the wall are much higher than those corresponding with the velocity slope at the boundary calculated from the known viscosity of air and the measured friction. In order to obtain more definite evidence on this point, the possibility of a a calibration of the Pitot tube in a current of air in which the distribution of velocity up to the boundary was known, was re-examined, and in view of the success which had attended the use of the new form of Pitot tube, it was decided to attempt the fitting of a tube of this

Table III.—No. 2 Pitot in 12·7 cm. Pipe.

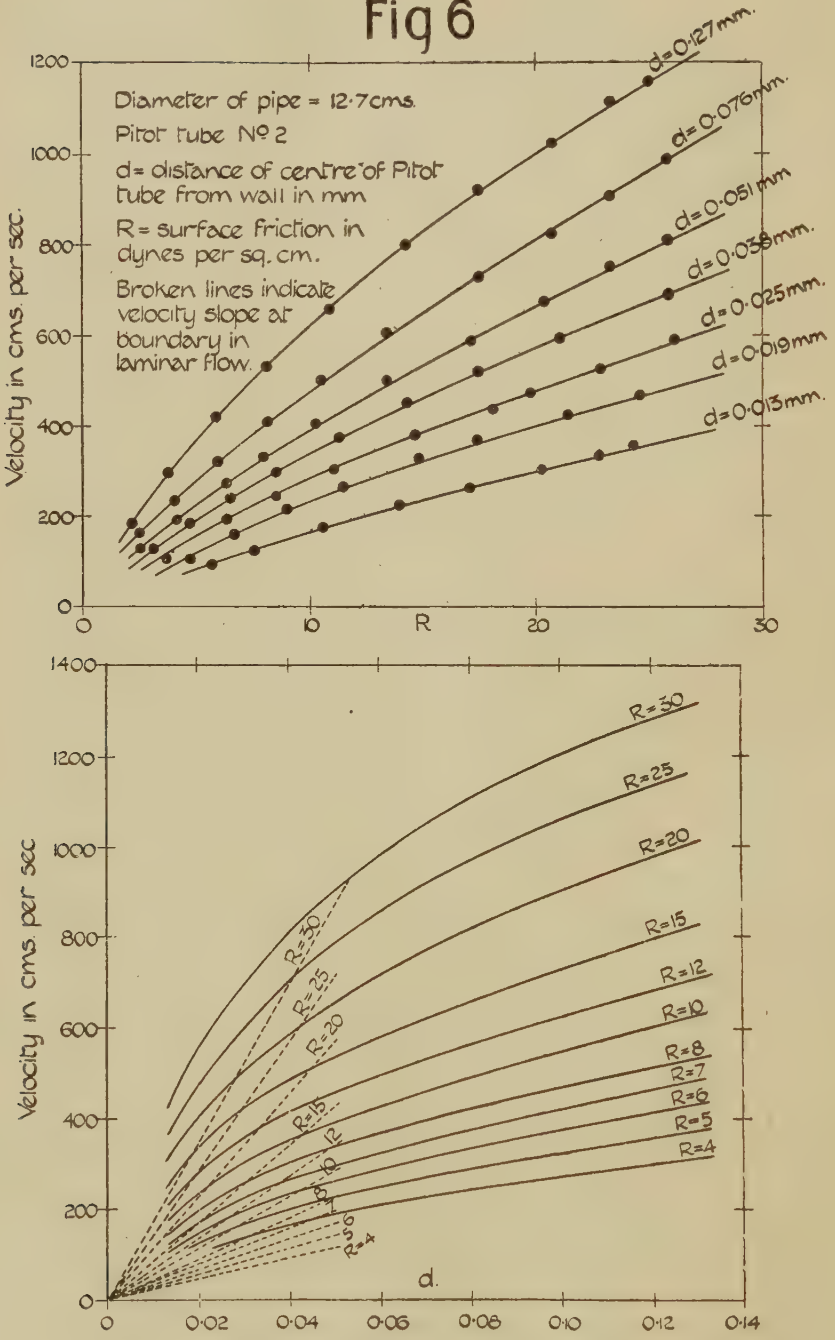
d = 0·127 mm.		d = 0·076 mm.		d = 0·051 mm.		d = 0·038 mm.		d = 0·025 mm.		d = 0·019 mm.		d = 0·013 mm.	
v. cm. per sec.	R. dynes per sq. cm.	v. cm. per sec.	R. dynes per sq. cm.	v. cm. per sec.	R. dynes per sq. cm.	v. cm. per sec.	R. dynes per sq. cm.	v. cm. per sec.	R. dynes per sq. cm.	v. cm. per sec.	R. dynes per sq. cm.	v. cm. per sec.	R. dynes per sq. cm.
185	2·16	165	2·52	130	2·52	130	3·02	105	3·74	107	4·69	93	5·59
295	3·78	235	4·01	190	4·10	185	4·69	195	6·31	160	6·67	125	7·84
420	5·86	320	6·00	270	6·27	240	6·53	245	8·47	220	8·97	175	10·6
530	8·11	410	8·17	330	7·94	295	8·51	305	11·1	265	11·5	215	14·0
660	10·9	500	10·5	405	10·3	375	11·3	380	14·7	330	14·9	260	17·1
800	14·3	610	13·4	500	13·4	455	14·4	435	18·1	370	17·4	300	20·2
920	17·5	730	17·2	590	17·1	520	17·5	470	19·8	425	21·4	335	22·8
1025	20·8	825	20·3	675	20·4	595	21·1	525	22·9	470	24·6	360	24·3
1115	23·3	910	23·3	750	23·3	695	25·9	590	26·1				
1160	25·0	980	25·8	810	25·8								

d = distance of centre of Pitot from wall.

v = surface speed.

R = friction.

Fig 6


Diameter of pipe = 12·7cms.
Pitot tube № 2
d = distance of centre of Pitot tube from wall in mm
R = surface friction in dynes per sq. cm.
Broken lines indicate velocity slope at boundary in laminar flow.
d=0·127mm.
d=0·076mm.
d=0·051mm
d=0·038mm.
d=0·025mm.
d=0·019mm
d=0·013mm.
Velocity in cms. per sec.
1200
1000
800
600
400
200
0
0
10
R
20
30
R=30
R=25
R=20
R=15
R=12
R=10
R=8
R=7
R=6
R=5
R=4
R=30
R=25
R=20
R=15
12
10
8
7
6
5
R=4
Velocity in cms. per sec
1400
1200
1000
800
600
400
200
0
0
0·02
0·04
0·06
0·08
0·10
0·12
0·14
d.

form to a pipe of about 0·25 cm. diameter. The construction of this attachment, it is needless to say, required considerable skill and accuracy, and much credit is due to Mr. H. G. Pincott of the Mechanical Staff of the Engineering Department for the success with which it was carried out. The diameter of the pipe used was 0·269 cm., the Pitot tube (here referred to as No. 3) was 1·27 mm. wide and the upper wall had a thickness of 0·05 mm.

In the experiments with this pipe the outlet end was connected by a rubber tube to a gas holder of which the rate of displacement could be varied by means of the tension in the supporting cord. It was possible, therefore, in these tests to make a series of observations at a constant value of the surface friction and there was no necessity to reduce the actual observations by preliminary plotting to obtain these results. The first series of tests were made with the Pitot tube at a given distance from the wall and over as large a range in the rate of flow as possible (Table IV). These observations were then repeated for another distance of the tube from the wall. The results are shown plotted in fig. 7, in which the ordinates of the plotted points are the speeds indicated by the Pitot tube and the abscissæ the rates of mean flow. In the same figure are also plotted the values of the surface friction obtained from the fall of static pressure in the pipe (Table V). It will be seen that at rates of flow below the critical, when the flow over the whole pipe was streamline in character, the plotted points in the velocity curves

Table IV.—No. III Pitot in 0·269 cm. Pipe.

$d = 0{\cdot}064$ mm.		$d = 0{\cdot}038$ mm.	
Mean speed, V.	Surface speed, *v*.	Mean speed, V.	Surface speed, *v*.
cm. per sec.	cm. per sec.	cm. per sec.	cm. per sec.
255	95	315	76
480	155	710	160
575	190	1000	215
780	240	1345	285
960	285	1420	300
1210	350	1460	295
1385	390	1555	310
1465	410	1575	320
1490	450	1635	415
1535	525	1665	510
1590	645	1700	560
1690	730	1830	630
1820	815	1970	695
2125	1010	2105	785
2415	1195	2290	855
2695	1370	2350	940
2900	1525	2400	940
—	—	2535	1015
—	—	2665	1080
—	—	2900	1230

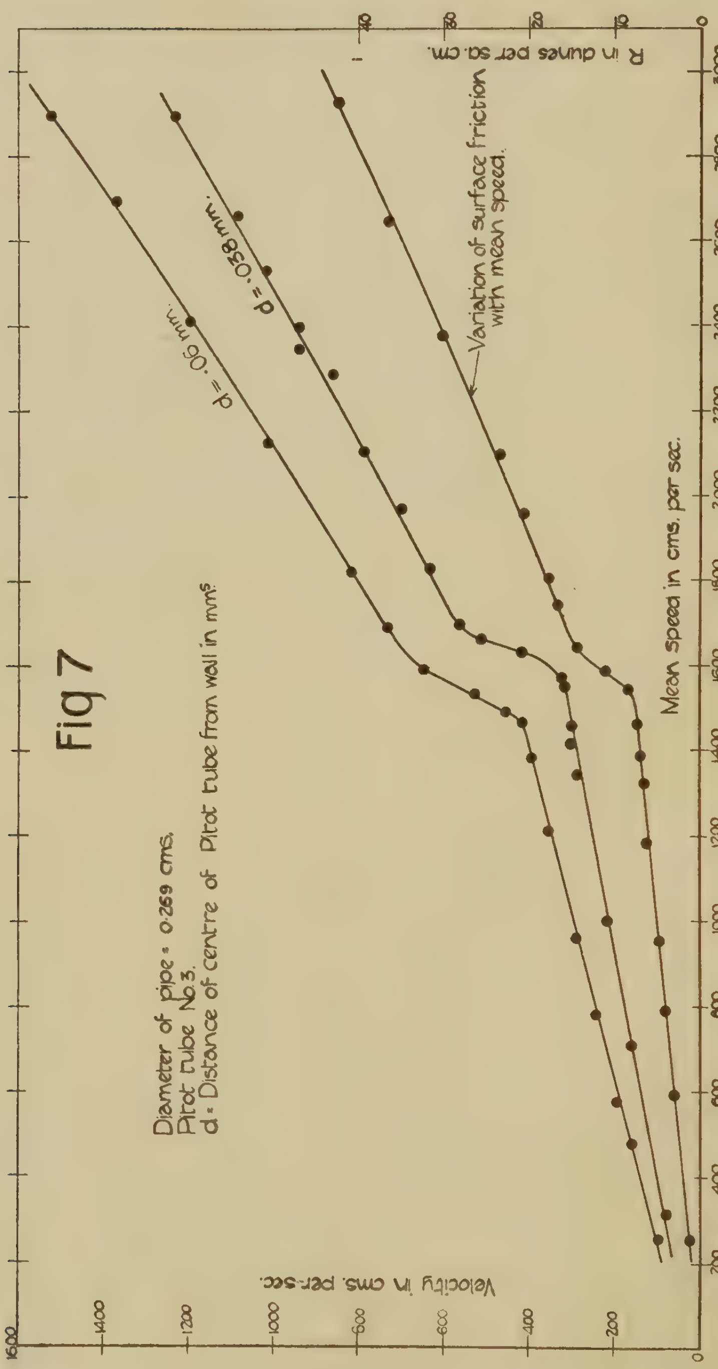


Fig 7

Diameter of pipe = 0·269 cms.
Pitot tube No. 3.
d = Distance of centre of Pitot tube from wall in mms.
d = ·06 mm.
d = ·038 mm.
Variation of surface friction with mean speed.
Velocity in cms. per-sec.
Mean speed in cms. per sec.
R in dynes per sq. cm.
0
200
400
600
800
1000
1200
1400
1600
1800
2000
2200
2400
2600
2800
3000
10
20
30
40

Table V.—No. III Pitot in 0·269 cm. Pipe.

Mean speed, V.	Friction, R.	Mean speed, V.	Friction, R.
cm. per sec.	dynes per sq. cm.	cm. per sec.	dynes per sq. cm.
255	1·15	1590	10·9
595	2·80	1645	14·3
790	3·88	1745	16·5
955	4·60	1810	17·6
1185	6·13	1960	20·6
1325	6·40	2100	23·4
1390	6·76	2380	30·1
1465	7·15	2650	36·4
1545	7·64	2925	42·4
1570	9·66		

Table VI.—No. III Pitot in 0·269 cm. Pipe.

Pitot tube opening.	Mean speed = 955 cm. per sec.		Mean speed = 570 cm. per sec.		Mean speed = 370 cm. per sec.	
	Surface speed, *v*.	Calculated effective distance.	Surface speed, *v*.	Calculated effective distance.	Surface speed, *v*.	Calculated effective distance.
mm.	cm. per sec.	mm.	cm. per sec.	mm.	cm. per sec.	mm.
0·0254	160	0·0559	—	—	—	—
0·0508	200	0·0737	125	0·0762	80	0·0737
0·0762	225	0·0813	150	0·0914	90	0·0864
0·1016	260	0·0940	170	0·1041	105	0·0940
0·1270	300	0·1092				
0·1524	310	0·1143	205	0·1271	135	0·1271
0·1778	345	0·1271				
0·2032	370	0·1372	245	0·1549	160	0·1524
0·2286	395	0·1473				
0·2542	420	0·1549	280	0·1752	185	0·1778
0·3048	465	0·1752				
0·3302	—	—	325	0·2083	215	0·2010
0·3556	530	0·2006				
0·4064	—	—	370	0·2413	250	0·2463

lie on straight lines passing approximately through the origin. It may be concluded, therefore, that these calculated speeds are the values of the speeds existing at a certain point near the boundary, although this point may not be the geometrical centre of the Pitot tube orifice. The desired calibration of the Pitot tube appeared, therefore, to be a simple matter, and was made as follows. For a certain value of the mean rate of flow below the critical value, a series of readings of the Pitot tube pressures were made at different distances of the geometrical centre of the Pitot tube from the wall (Table VI). From the equation of the distribution of velocity in streamline flow, $V = V_c(1-r^2/a^2)$, the values of r were calculated for each value of V obtained from the observations. Points were then plotted whose ordinates were the values of $(a-r)$, and whose abscissæ were the corresponding distances of the geometrical centre of the Pitot tube from the wall. This process was repeated for different values of the mean flow, all below the critical value, and the mean curve through all the plotted points was taken to be the calibration curve for the Pitot tube. This curve is shown in fig. 8. It will be seen that for openings of the order of 0·3 mm. the assumption that the calculated speed is that which exists at the geometrical centre of the orifice is not greatly in error, but that when the opening is of the order of 0·075 mm., the interference with the flow is so considerable that the calculated speed is that which exists at the edge of the Pitot tube furthest from the wall.

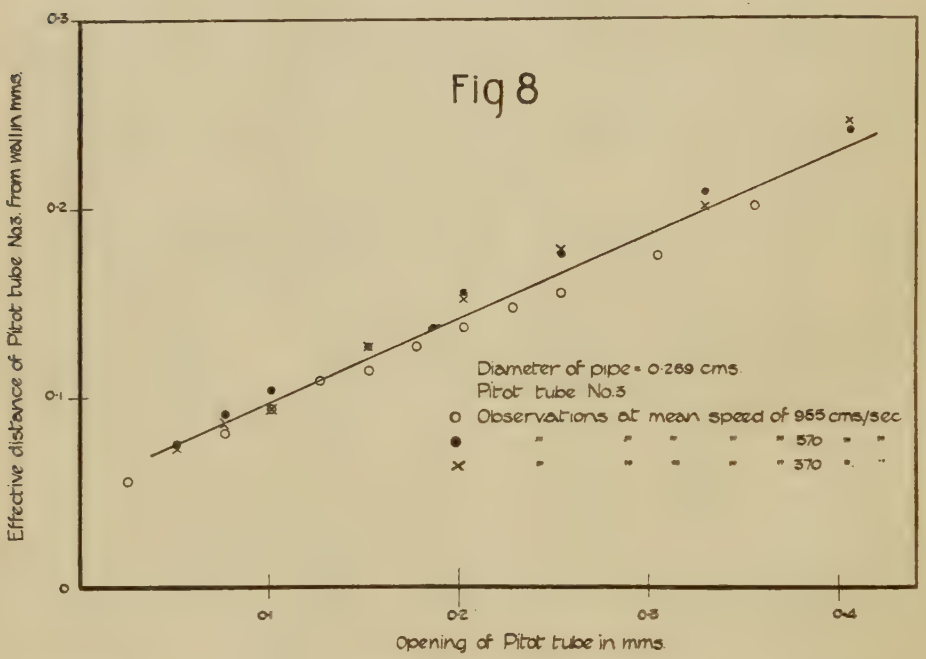


Fig 8

A series of observations were then made at known values of the surface friction, and with the centre of the Pitot tube at different distances from the wall (Table VII). The speeds calculated from these observations are shown plotted in two methods in fig. 9. On the left-hand side of the figure, the abscissæ of the points are the distances of the centre of the Pitot tube from the wall, and, on the right-hand side, the abscissæ are the "effective distances" of the Pitot tube from the wall, as scaled off from the calibration curve of fig. 8.

Table VII.—No. III Pitot in 0·269 cm. Pipe.

Mean velocity = 2400 cm. per sec. Mean friction = 30·4 dynes/sq. cm.			Mean velocity = 2025 cm. per sec. Mean friction = 23·3 dynes/sq. cm.			Mean velocity = 1810 cm. per sec. Mean friction = 17·2 dynes/sq. cm.		
Mean distance. mm.	Effective distance. mm.	Surface speed. cm. per sec.	Mean distance. mm.	Effective distance. mm.	Surface speed. cm. per sec.	Mean distance. mm.	Effective distance. mm.	Surface speed. cm. per sec.
0·127	0·159	1625	0·178	0·198	1655	0·203	0·216	1470
0·076	0·118	1300	0·165	0·188	1585	0·165	0·188	1325
0·051	0·097	1090	0·152	0·178	1525	0·127	0·158	1160
0·038	0·084	970	0·127	0·159	1405	0·102	0·137	1040
0·025	0·071	890	0·102	0·140	1275	0·076	0·117	890
0·013	0·056	795	0·076	0·118	1105	0·051	0·094	710
0·006	0·046	675	0·051	0·097	900	0·038	0·083	610
—	—	—	0·038	0·084	785	0·025	0·071	535
—	—	—	0·025	0·071	655	0·013	0·055	470
—	—	—	0·013	0·056	615	0·006	0·044	440

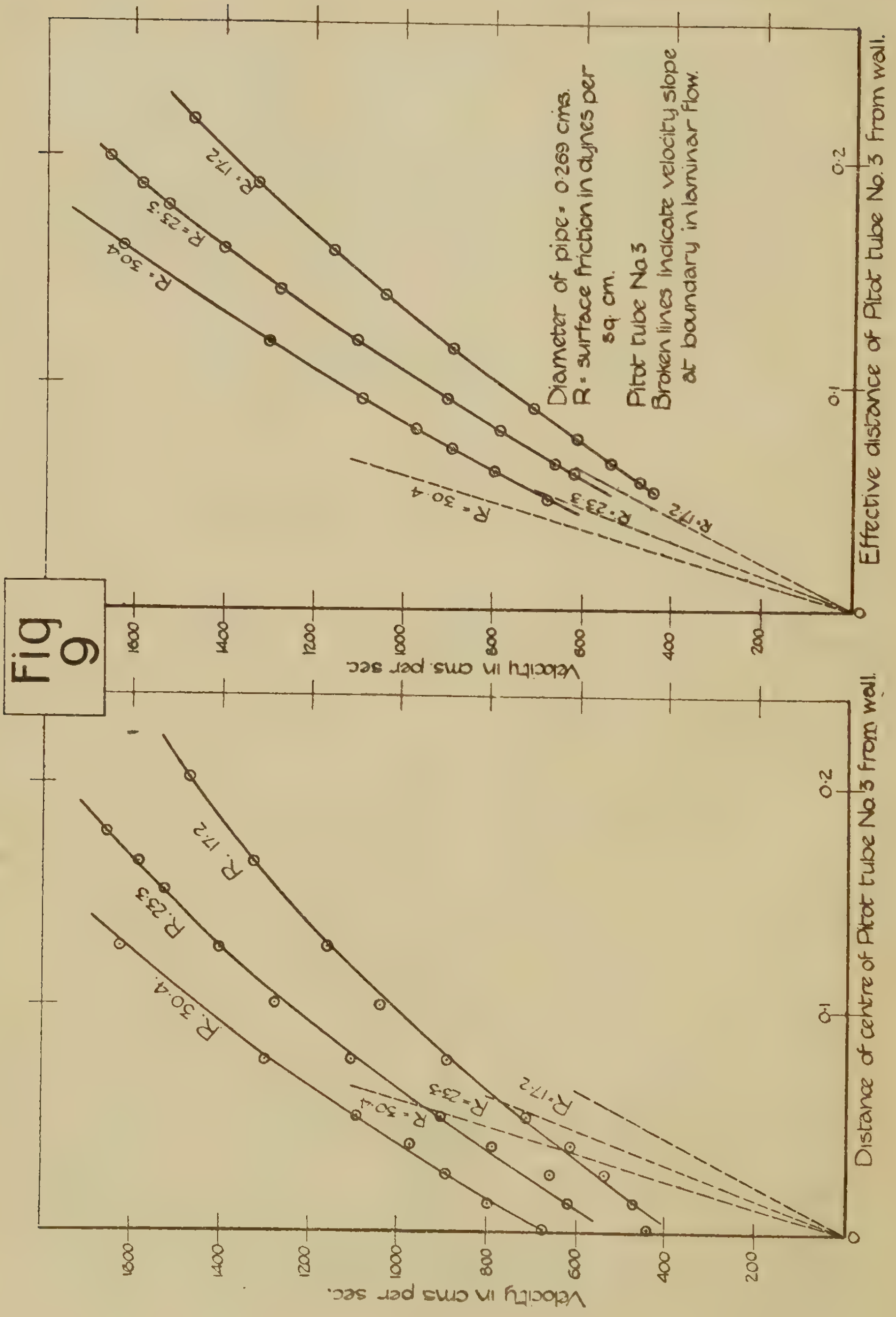


Fig 9

Diameter of pipe = 0·269 cms.
R = surface friction in dynes per sq. cm.
Pitot tube No 3
Broken lines indicate velocity slope at boundary in laminar flow.
R. 17·2
R = 23·3
R. 30·4
R = 30·4
R = 23·3
R = 17·2
R. 17·2
R. 23·3
R. 30·4.
R = 30·4
R = 23·3
R = 17·2
Effective distance of Pitot tube No. 3 from wall.
Distance of centre of Pitot tube No 3 from wall.
Velocity in cms. per sec.
Velocity in cms. per sec.
0
0·1
0·2
200
400
600
800
1000
1200
1400
1600

It will be obvious, of course, that the application of this calibration curve to velocities indicated by the Pitot tube when in corresponding positions, but with the flow turbulent, is open to criticism, since this would involve the assumption that the magnitude of the interference for any given distance from the wall is the same for turbulent motion as for laminar motion. This criticism would certainly need very careful consideration if the degree of turbulence at these positions were of the same order as that at the centre of the pipe. It is clear, however, from the curves of fig. 4, that the turbulence is greatly diminished in intensity at distances from the wall as small as those under consideration, from the fact that in this region the surface friction is proportional to V^n, where V is the observed speed, and n is little in excess of unity. For this reason, it is here assumed that the calibration curve of fig. 8 can be applied in experiments with values of flow above the critical with reasonable accuracy.

On examination of the two sets of curves, it will be seen that the effect of the correction for interference in the slope of the curves at distances from

Fig 10

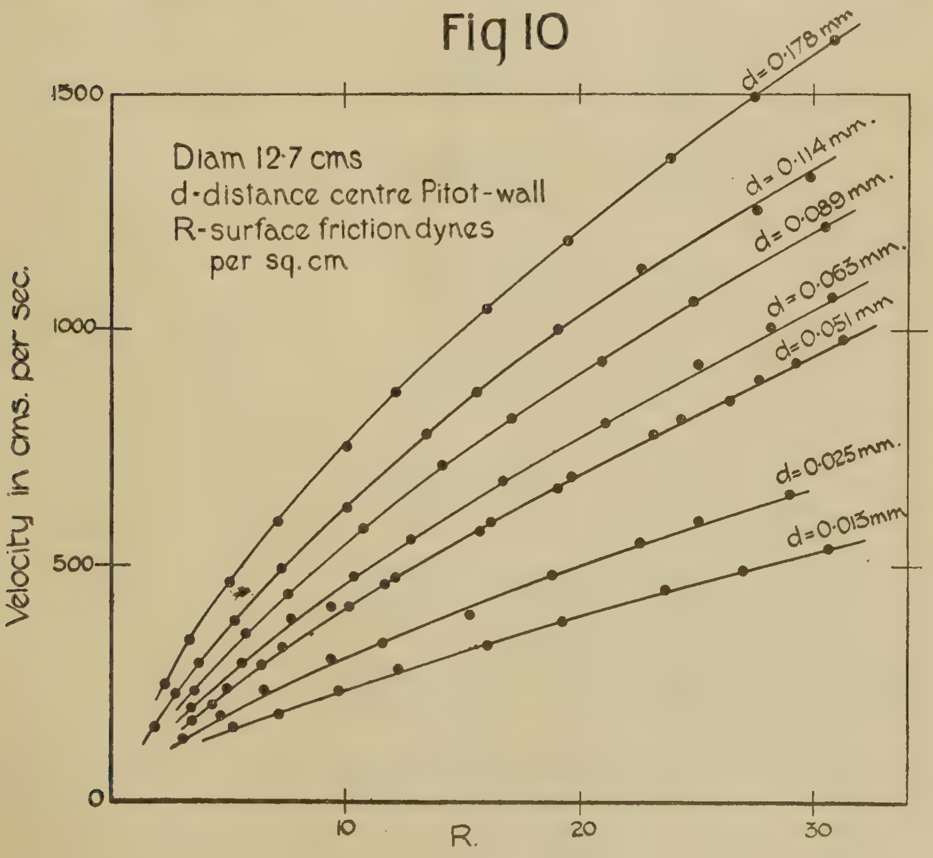


Table VIII.—No. III Pitot in 12·7 cm. Pipe.

$d = 0 \cdot 178$ mm.		$d = 0 \cdot 114$ mm.		$d = 0 \cdot 089$ mm.		$d = 0 \cdot 063$ mm.		$d = 0 \cdot 051$ mm.		$d = 0 \cdot 025$ mm.		$d = 0 \cdot 013$ mm.	
v. cm. per sec.	R. dynes per sq. cm.	v. cm. per sec.	R. dynes per sq. cm.	v. cm. per sec.	R. dynes per sq. cm.	v. cm. per sec.	R. dynes per sq. cm.	v. cm. per sec.	R. dynes per sq. cm.	v. cm. per sec.	R. dynes per sq. cm.	v. cm. per sec.	R. dynes per sq. cm.
								(i)					
245	2·30	155	1·85	235	3·5	195	3·4	170	3·45	130	3·11	155	5·2
340	3·38	225	2·75	355	5·8	290	5·6	240	5·0	180	4·7	185	7·2
465	5·14	290	3·75	440	7·6	370	7·6	325	7·3	235	6·5	235	9·8
595	7·1	385	5·3	580	10·8	475	10·4	410	10·1	300	9·4	280	12·3
755	10·1	495	7·35	715	14·2	555	12·8	475	12·2	335	11·6	330	16·1
870	12·1	625	10·1	815	17·1	680	16·7	595	16·3	395	15·4	385	19·3
1045	16·1	780	13·5	935	21·0	805	21·1	690	19·7	480	18·9	450	23·7
1190	19·5	870	15·6	1060	24·9	925	25·1	810	24·3	550	22·6	490	27·0
1365	23·9	1000	19·1	1220	30·5	1005	28·2	895	27·7	595	25·1	535	30·7
1495	27·5	1130	22·7	—	—	1070	30·8	980	31·3	655	29·0		
1615	30·9	1260	27·7										
—	—	1325	29·9										
								(ii)					
								205	4·15				
								290	6·4				
								420	9·4				
								460	11·7				
								575	15·8				
								665	19·1				
								780	23·2				
								850	26·4				
								930	29·3				

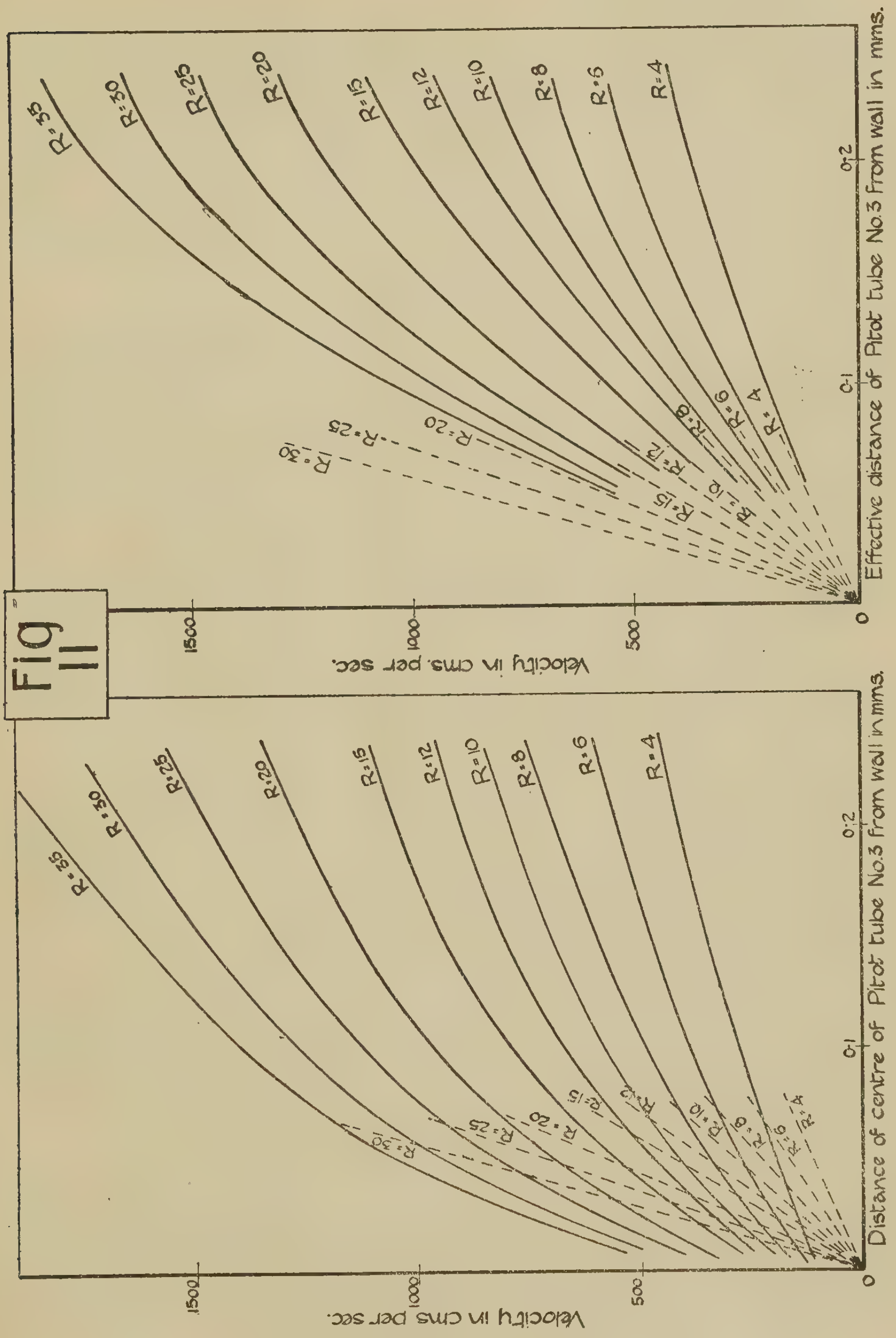


Fig. 11
R=35
R=30
R=25
R=20
R=15
R=12
R=10
R=8
R=6
R=4
0
0·1
0·2
500
1000
1500
Velocity in cms. per sec.
Effective distance of Pitot tube No. 3 from wall in mms.
Distance of centre of Pitot tube No. 3 from wall in mms.

the wall of the order of 0·3 mm. is practically negligible, as would be expected, but that, at distances of the order of 0·05 mm., the slopes, when corrected for interference, are considerably increased, and approximate fairly closely to the values which would exist in laminar flow with the same surface friction. Further, there is no indication of the existence of any slip at the boundary. It was concluded, therefore, that in the turbulent flow of air through this small pipe at speeds of about double the critical speed, the exploration of the flow near the boundary by means of a fine Pitot tube showed unmistakably the existence at the boundary of a finite layer of fluid in laminar motion and having zero velocity at the boundary.

As the rates of flow in the experiments in the 0·269 cm. pipe were not greatly in excess of the critical value, it was decided to repeat the experiments in the 12·7 cm. pipe, and for this purpose the No. 3 Pitot tube was transferred to this pipe and a series of observations made with it at fairly high rates of flow (Table VIII). The results are shown plotted in fig. 10 and the values of the velocities reduced from these curves to show the variation of the speed at constant values of the surface friction are shown in fig. 11, in the same way as the results illustrated in fig. 9, *i.e.*, on the left are shown the curves of velocity variation with distance of centre of Pitot tube from wall, and on the right the same results corrected for the interference, on the assumption that this is unaffected by the radius of curvature of the walls. This assumption may not be true to a high degree of accuracy, but it is obviously the only one which could be made under the circumstances.

It will be seen that when the correction for interference is made, the curves of velocity distribution tend to a definite slope at the boundary which is identical with that which would exist in a layer of fluid in laminar motion and having the same surface friction, a result which is in agreement with that obtained from the observations in the 0·269 cm. pipe.

The general conclusions which are arrived at from the whole series of experiments here described are that in turbulent motion there exists at the boundary a layer of fluid of finite thickness, which is in laminar motion, and which has zero velocity at the boundary. Expressing this in symbols, the boundary condition is

$$\mu \mathrm{Lt}\left(\frac{dv}{dx}\right)_{x \to 0} = \mathrm{R},$$

where the origin is taken in the boundary and x is measured along the normal, v is the velocity parallel to the boundary, μ is the coefficient of viscosity of the fluid, and R is the intensity of the surface friction.

A Re-examination of the Light scattered by Gases in respect of Polarisation. I.—Experiments on the Common Gases.

By Lord Rayleigh, F.R.S., Professor of Physics, Imperial College of Science, South Kensington.

(Received June 1, 1920.)

Introduction.

In an earlier paper* I showed that the light scattered by gases free of dust was not perfectly polarised, but that a residual defect of polarisation remained, which was characteristic for each gas. This was an entirely new field of investigation, and the experimental methods for detecting and measuring a very minute effect had to be worked out. As is the universal experience, many improvements suggested themselves in the course of the work, and after an interval it was decided to repeat a part of it again, with many modifications in detail, designed to give the most accurate numerical results that seem at present obtainable. This has now been done, with results which, speaking generally, confirm the earlier investigation, except in one important particular.

It was decided to limit the present investigation to the permanent gases, thus excluding the vapours of organic substances. The latter are inevitably absorbed by the blacking which it is necessary to use on the inside of the vessel, and when the substance under investigation is changed they may come off and give rise to contamination. Moreover, there is the tendency of some of these substances to form fogs under the influence of light. It would have been premature to include them in a first attempt to establish accurate methods. Pioneer determinations were given in the former paper, and are believed to be substantially correct.

The great difficulty in this work is the feebleness of the light. In considering how the former methods could be improved upon, it appeared that the chief possibility remaining open was to use a broader beam of exciting light, so as to photograph laterally a deeper layer of gas giving secondary emission. This entails a much larger vessel than that used before, not only to admit the larger beam, but also for the avoidance of scattered light. The vessel formerly used, it will be remembered, was in the form of a cross, the primary beam passing along one direction and the lateral scattering being observed in the perpendicular one. If the conditions are to remain as favourable for the avoidance of stray light, it is necessary to preserve geometrical similarity. The beam formerly used was only ½ inch broad. It was desired in the present work to use a 4-inch beam. This would require the vessel to be magnified eightfold in linear dimensions, which would mean 1 foot diameter and arms of 12 feet and 18 feet. These dimensions are practically prohibitive on the laboratory scale, and it was necessary to cope with conditions much less favourable than before for the avoidance of stray light. After much experimenting, the desired result was attained in a vessel of moderate dimensions.

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* 'Roy. Soc. Proc.,' A, vol. 95, p. 155 (1918).

§ 2. *Black Background.*

The most important point to be attended to is the way in which the far end of the vessel (away from the camera) is constructed. This necessarily forms the background, against which the faint light under investigation is to be observed, and it must be arranged so as to send back exceedingly little stray light. The requirements are very severe. The back surface must not be luminous enough to produce the faintest photographic impression in an exposure of 24 hours or more with the most sensitive plates and the most rapid lens, and this in the neighbourhood of the beam from a powerful arc.

No ordinary blacking of the surface was found adequate, having regard to the comparatively short distance at which it had to be placed. The best that can be done in this way, so far as my experience goes, is to smoke the surface over a gas-jet, but this is far from good enough. Blacking of any kind diffuses some light in all directions, and, amongst others, in the particular direction which is harmful, *i.e.*, towards the lens. On the other hand, a perfectly polished surface reflects the light in one direction only, and this may be arranged to be a direction where it is harmless.

The first expedient tried was to place a piece of ruby glass obliquely in the tube, so that the reflexion from it would be towards the side wall of the vessel. This was a great improvement when compared with blacking, but suffered from several defects.

Ruby glass is full of small particles to which the colour is due. These scatter some light diffusely from the surface, and this light was found to be more actinic than might have been expected, probably because it comes from a layer so near the surface that absorption of blue light is incomplete. What is to be aimed is, of course, a glass which is so coloured as to absorb and get rid of any actinic light which enters it, without scattering anything back. A study of various glasses showed that deep green (coloured, I believe with chromium), combines photographic opacity with absence of scattering. Further, it was found that a fired surface was preferable to any polish that could be obtained. These conclusions were established by holding the glasses to be tested directly in a very powerful beam, and estimating the photographic importance of the scattered light by a blue glass held over the eye.

But a single oblique plate of glass has another defect. The surface reflects an appreciable percentage of the incident light to the side wall, and this light, together with any that may fall on the side wall directly, is partially reflected back by the glass plate, and thus gets back to the camera. Even this effect was appreciable. It was met by using a curved horn blown from green glass by Messrs. Powell. Any light which fell into the mouth of the horn was reflected internally from side to side and soon lost completely (fig. 1). The internal blown surface was very good for the purpose.

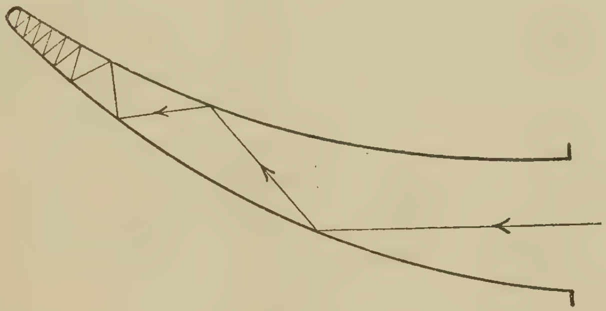

FIG. 1.

The horn was covered outside with black paint, and wrapped in black cloth as an additional precaution. Such a background appears extraordinarily black, even when a powerful arc shines right into it. It is instructive to compare it under these conditions with a piece of black velvet, which seems by comparison a brilliant object.

§ 3. *Limitation of Photographed Area.*

Another point to be considered is how the illuminated area which is photographed on the plate is to be defined or limited. In the former work this was done by taking advantage of the limited cross-section of the beam itself, the outline of which was focussed upon the plate. With a great increase of the depth illuminated, this is no longer satisfactory, for if the nearer parts of it are in focus, the distant ones cannot be so, and the diffuse edges of the two oppositely polarised images would overlap, unless indeed these two images were widely separated, which is undesirable on other grounds. For this reason, a rectangular diaphragm was used, which was backed by the layer of luminous gas. A rather larger diaphragm was placed nearer the primary beam and protected the final diaphragm from any danger of being grazed by the primary beam, which would have produced a very harmful illumination of its edges.

§ 4. *Polarising Prisms.*

In the former investigation, the two images formed by a double image prism suitably oriented were assumed to have intensities in the same ratio as the polarised components of the scattered light. These intensities were approximately equalised by an absorbing screen placed over the plate, to cover the denser image, and the measurement consisted, briefly, in finding an appropriate screen out of a series of graduated density, the absorbing power of which was known. This method is advantageous in the saving of light, but obviously does not lend itself very well to anything beyond rather rough measurements. In the present work, a large nicol was employed in front of the double image prism, to equalise the two beams, according to a method used by Cornu and by my father, for examining the polarisation of the sky. This method has the great advantage of readily allowing continuous adjustment, as close as may be desired. The objection to it is the loss of light, but this could be tolerated with the better illumination now used, and the longer exposures which were practicable when the field of work had already been surveyed. The case of helium, however, is an exception in this respect, and will be treated separately.

Preliminary tests showed that, starting with unpolarised light, the double image prism did not produce two images of equal intensity within the desired limits of accuracy. Evidently, therefore, the ratio of intensities obtained with partially polarised light could not be taken as a true measure of the constitution of the light. Further, from other tests, there was reason to suspect that a nicol prism placed over the camera lens did not affect the two images according to the simple law of $\tan^2\theta$—indeed, with an oblique ended nicol, this is not to be expected; but the discrepancies seemed greater than anticipated. For these reasons, a method was used which avoids any assumptions about the behaviour of the polarising prisms.

This method depends on an empirical adjustment beforehand. Suppose, for instance, that we wish to determine whether the original polarisations have intensities in the ratio $1:n$. The nicol must be set in such a position that it would equalise the intensities under these circumstances. To set the nicol, unpolarised light from a steady source is used, but, by covering up one of the images with a screen near the plate, we may expose them separately, and thus arrange for the horizontally vibrating component to receive n times as much light as the vertically vibrating one. This is most conveniently attained by diaphragming the camera lens to $1/n$th aperture between the exposures. The diminution of aperture, it is true, reduces the light *after* passing the prisms, but, for a given exposure (one polarisation only), its effect is obviously the same as if some means of reducing the original source to $1/n$th intensity had been employed during that exposure.

It was found most convenient in practice not to cover one of the images, in view of their small size and nearness together, but to make two separate exposures on different parts of the plate, each showing a pair of images. The pair made with the smaller aperture was, of course, the less intense. The nicol was adjusted until the weaker image of one pair was made equal to the stronger image of the other pair, using diaphragms in a given ratio. The order of the exposures and the displacement of the plate was, of course, arranged so as to bring these two images to be equalised side by side on the negative.

It was found that the brightest image, *i.e.*, the strong image from the large aperture, tended to produce halation on the plate, which would, of course, give rise to systematic error. This was only partly got rid of by using backed plates, and it was necessary, therefore, to prevent the strong image (which is not used in the measurement) from falling on the plate at all. This was achieved by a suitable screen or stencil of thin ebonite in contact with the film. The obscuring strips of ebonite were spaced ¾ inch apart, the exact distance through which the plate was moved when making a new pair of exposures (four such pairs were made on each plate). Thus in each case there was an ebonite strip in position to obscure the strong image, leaving the other three.

The method of calibration adopted is subject in addition to a source of error which was not sufficiently appreciated when this method was designed. The error arises from *false light*, *i.e.*, light reflected or scattered from the various surfaces of the lens and polarising prisms. This is of no practical importance when the only images which reach the camera are of approximately equal brightness, as in making the adjustment with light scattered by a gas. When, however, the calibration is made, the strong image is surrounded by a glare which extends around it with intensity diminishing as we proceed outwards. Although the strong image itself is screened off by the ebonite strip, the glare around it reaches the plate, and is superposed in varying degrees on the two images of much less intensity which are to be equalised, thus making the apparent equality illusory. It appears impracticable to eliminate this source of error altogether, and all that can be done is to allow for it as well as possible. The nicol is set so as to give the best extinction attainable for the weaker image, and the calibration process carried out much as usual, except that the smaller diaphragm is now to be chosen, so that the strong (now the only) image given by it is equal in intensity to the false light which falls where the weaker (now extinguished) image for the larger diaphragm would have been. Practically, the exact size of diaphragm must be found by interpolation. In this way it was determined that the weaker image had a spurious apparent intensity equal to 0·677 per cent. of the stronger one, when its intensity should have been zero. It was assumed that this spurious addition remained the same for all the not very wide range of angular positions of the nicol that were used, and a subtractive correction was applied accordingly. This procedure is not wholly satisfactory, but the need for it was not discovered until the present section of the work had been considered finished; and no better method of making the correction suggested itself.

This method of calibrating by two exposures requires the use of a light whose constancy may be depended upon. A "Pointolite" lamp supplied by a storage battery *exclusively reserved for it*, answered this purpose.

§ 5. *Comparison of Photographs.*

In the earlier work ordinary photometric methods were used for testing whether the two images given by the double image prism had been successfully equalised, so as to give equal photographic effect. I was dissatisfied with the sensitiveness of this method, which as I applied it, at least, did not give a sharp enough test of equality.

In later experiments a photo-electric method of comparison has been used which has proved in practice far easier and less fatiguing. The arrangements are shown in fig. 2. At A is a "Pointolite" lamp (enclosed tungsten arc) focussed by a lantern condenser, B, on a slit, C, in the metal plate, D. This slit measures 3 × 1 mm. at the upper surface of D, but the four edges which define it are bevelled, so as to give a larger aperture below, to allow passage to the diverging cone of rays. These rays fall on a photo-electric cell, E (potassium, in helium at a few mm. pressure) in circuit with a dry battery giving about 150 volts and a sensitive high resistance moving coil galvanometer. The negative under examination is placed film downwards on the plate, D, which is embedded flush in the top of a box enclosing the photo-electric cell, and protecting it from stray light (see the plan fig. 3, lettered to correspond with fig. 2). The images to be compared, HH, fig. 3 are brought successively over the slit, and the galvanometer deflection noted. There is an adjustable guide, FF (both figs.) for that edge of the negative which is perpendicular to the slit, and to the long dimension of the images. In changing to and fro from one image to the other, the correct central position over the slit is judged by eye, assisted in some cases by suitable ink dots on the negative (fig. 3). The point to be noted is which image gives the smaller

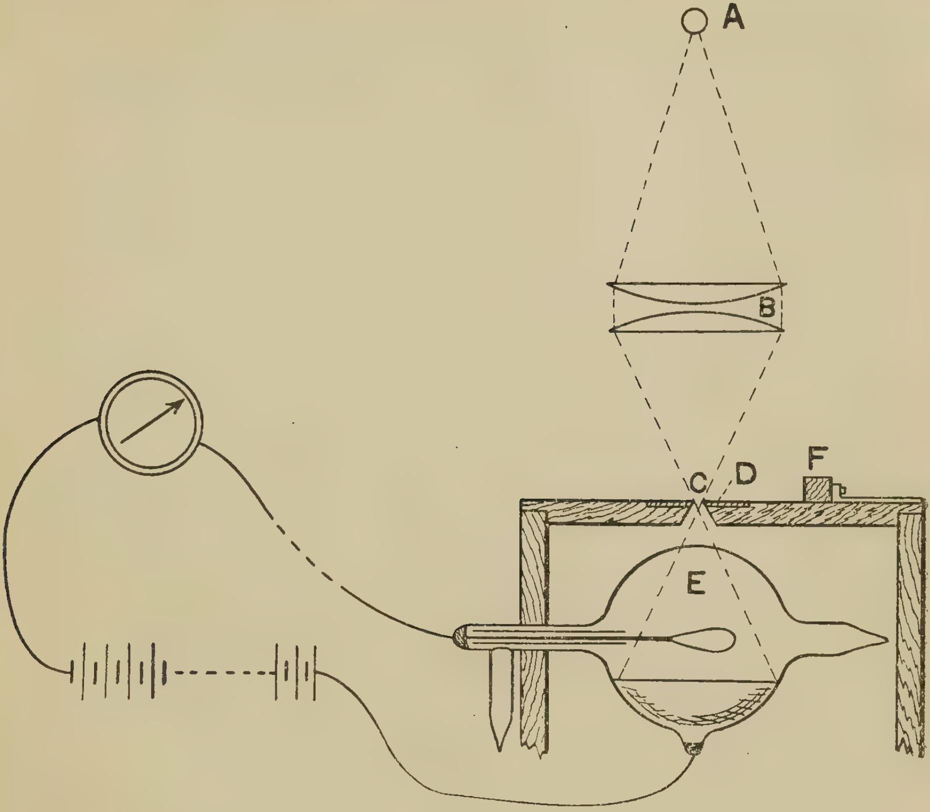

Fig. 2.

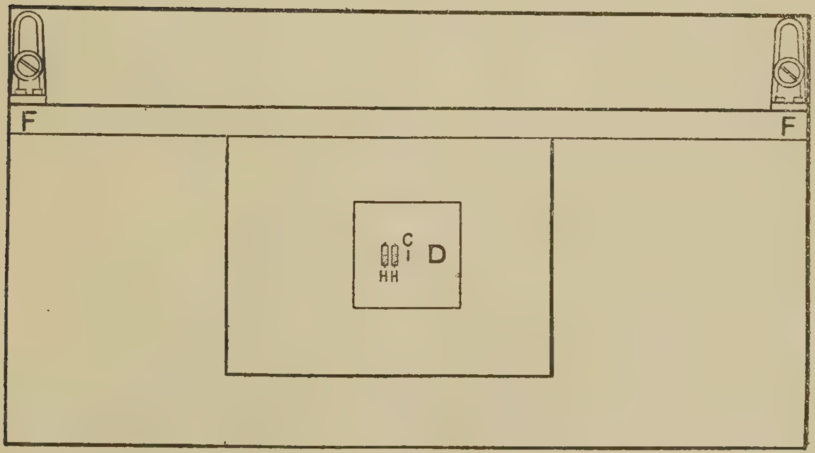

Fig. 3.

deflection, and is the more opaque. A number of alternate readings were taken and were usually in good agreement. The "Pointolite" lamp was of the "fixed focus" pattern; the more usual pattern, with a tungsten knob which moves as the lamp heats up, was found decidedly less satisfactory for this work.

The photometric arrangements ultimately adopted were very satisfactory, and with a given pair of images results which were much more concordant among themselves than those which were obtained when a second pair, taken under (apparently) the same conditions was substituted.

It was absolutely necessary to use for the "Pointolite" lamp a storage battery which was not in use at the same time for other work. When induction coils, motors, etc., were being used on the same battery hopeless irregularities were introduced.

The two images to be compared necessarily occupy different positions on the plate, and it is necessary, therefore, that the latter should be as uniform as possible, if accurate results are to be obtained. I tested ordinary photographic plates in this respect by fogging them by a few seconds' exposure to a distant candle, and after development, testing the opacity of different parts with the photo-electric apparatus. A serious lack of uniformity was found, and it was almost always easy to determine which of two closely contiguous portions was the denser: what was worse, there were occasional *precipices* on the plate, where very sudden differences of opacity occurred. Though it would be theoretically possible to eliminate this source of error by repetition, yet the process would have been most tedious and unsatisfactory. Eventually, at the suggestion of my friend, Prof. R. W. Wood, I used plates coated on plate glass, which proved very much more uniform, when tested in the same way. It appears that the irregularities of ordinary plates are due in the main to want of flatness in the glass, which causes the film to be of variable thickness. The plates used were specially prepared for me by the Kodak Company. The emulsion used was Seed 27 and Seed 30. The latter is the most suitable that I have been able to find for this work when great rapidity is the main essential.

Special attention has been paid to the question of the best density for the photographs. The object is to discriminate as closely as possible between two negatives of nearly equal density. If the exposure is very short, then, in the limit, neither image has perceptible density, and no discrimination can be made. Again, if the exposure is very long, both images are very dense, the total galvanometer deflection very small, and the difference of deflections imperceptible. An intermediate density is most favourable. Its value was investigated by a "Spurge sensitometer" kindly lent me by

Sir William Abney. This is, in effect, a collection of pinhole cameras with progressively increasing apertures, each having an area 1·25 times that of its predecessor. One of the plates to be used was exposed in this apparatus, to a diffused light and a series of graduated densities obtained. They were examined with the photo-electric cell, and it was found that beginning with the weakest image (barely visible), the change of deflection from one density to the next increased, reached a maximum, and then diminished. As might be expected, the difference remained fairly constant over a considerable part of the series in the neighbourhood of the maximum. If the opacity was such as to reduce the galvanometer deflection to 0·85 times the value obtained on the unexposed part of the plate, the best sensitiveness to change of exposure was practically attained, and continued nearly unaltered up to much denser exposures, such as would reduce the deflection to 0·3 of the bare film value. The densities used were kept within this range, and owing to the long exposures required in many cases, they were usually nearer the lower limit of opacity.

In using null methods of measurement, such as the balance or Wheatstone bridge, it is generally found best not to aim at precise adjustment, but to interpolate between positions on either side of the neutral point. In the present case where each observation involves a long photographic exposure, this is doubly advisable, for otherwise valuable material obtained with much trouble would be needlessly rejected.

Preliminary tests were made to locate the neutral point approximately, and then two positions, usually 0·5 degree on either side of it, were selected for taking the photographs. The departure from balance was measured on an arbitrary scale by the difference in galvanometer scale divisions for the two approximately equal images, when these were examined in the photo-electric apparatus. This difference was positive for one set of photographs, negative for the other. By interpolation the zero position was found.

§ 6. *Supply of Gas.*

The programme for accurate determinations of the ratio of polarisations included hydrogen, nitrogen, air, oxygen, carbon dioxide, and nitrous oxide.* All these, except air, were bought compressed in steel cylinders. In this way the use of acids, highly undesirable in the neighbourhood of valuable calcite prisms, was avoided. The apparatus was in each case exhausted, and filled up with the gas, and while the exposure was proceeding, a constant stream at the rate of about 500 c.c. per minute was maintained. In this way the gas actually under illumination was changed once a minute which greatly diminished any risk of error from the formation of a fog under the influence of light. No indication was ever noticed that this had occurred. The gas stream was dried with phosphorus pentoxide and filtered through closely packed cotton wool.

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* Work on the rare gases will be described later.

Careful consideration of the amount and character of impurity liable to be present in the commercial gases clearly shows that no sensible error could arise from this cause.

§ 7. *Arrangements for Observing Scattering.*

The apparatus (figs. 4, 5, 6) is shown natural size, the main brass tube, A, being 4 inches diameter. The rectangular ribbed castings, BC, were screwed and soldered to it. The exciting beam enters through the plate glass window at D. It is confined by the rectangular diaphragms F, G, and H. After crossing the main vessel and entering C it falls on the window E, smoked inside. The centering can be verified by observing the patch of light on this window.

The laterally scattered light was observed through the window, M. On looking through this window the diaphragm, L, was seen as a rectangular patch of bluish light on a black ground. The larger diaphragm, K, served merely to reduce the stray light that fell on the *edges* of *l*, and which tended to make these edges appear luminous as seen from M. W is the green glass horn already described. Its flat ground flange was cemented to the brass flange terminating H.

To avoid strain on the cement, W was further held in position by a metal ring, provided with three studs and nuts. A rubber ring acted as cushion to distribute the pressure uniformly on the outside of the glass flange.

P and Q are for the entrance and exit of a stream of gas.

R and S are the ends of the charcoal vessel attached to the apparatus for the purification of helium. T is the gauze distributor which is used in connection with the charcoal purification. The description of this part of the work is deferred for a later paper.

The metal parts were soldered together and covered with two successive coatings of stoved enamel, as used for bicycles, etc. The glass parts were attached to the metal by a cement of pitch and gutta-percha, somewhat harder than Chatterton's compound.

The air-tightness attained was remarkable. The vessel was exhausted and left in communication with the charcoal and with a MacLeod gauge. No leakage amounting to $\frac{1}{10}$ mm. had occurred after the lapse of two months.

As before, a hand-feed lamp was used with positive carbon horizontal and negative only slightly inclined to the vertical. "Kinarko" cinematograph

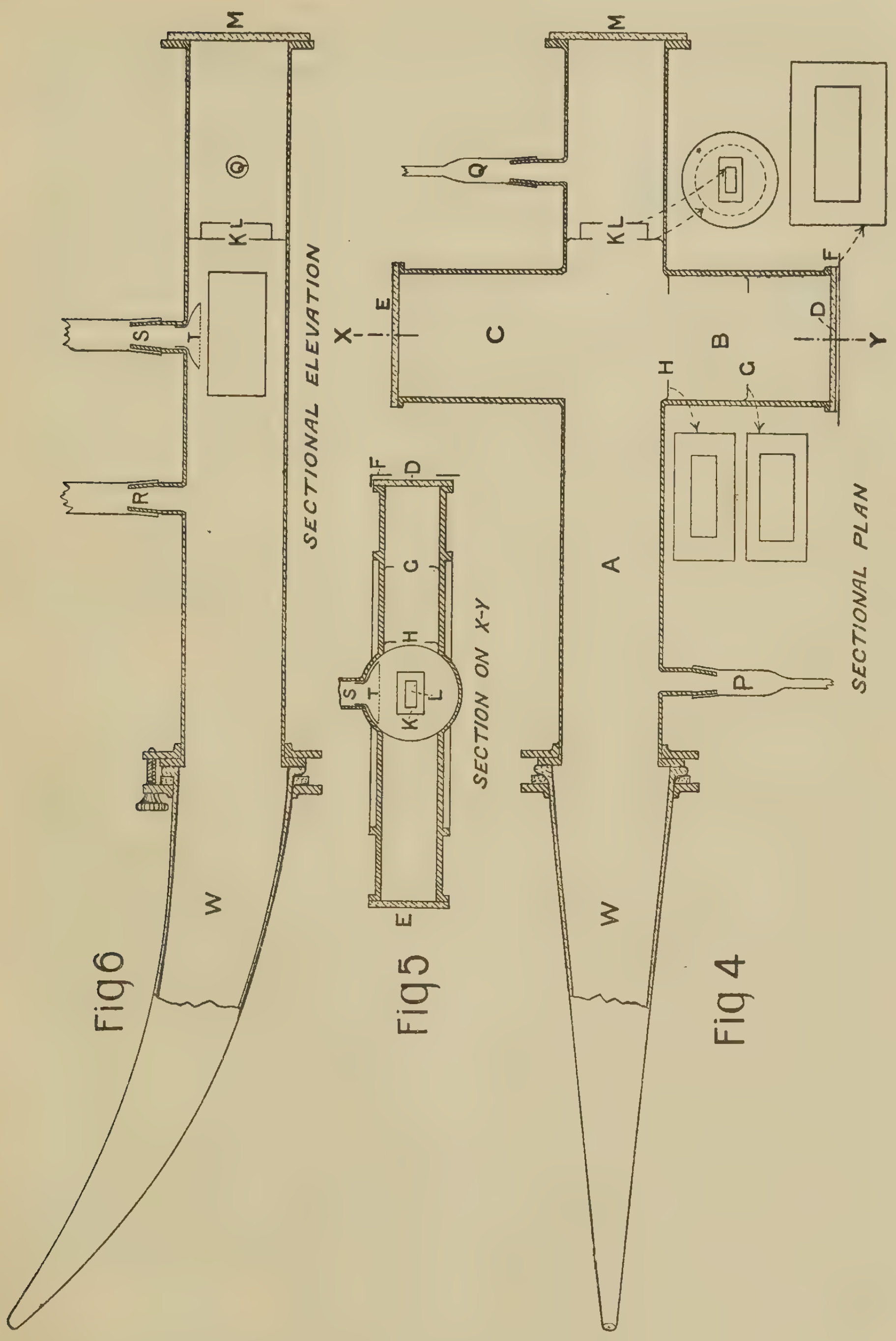
M
Q
K L
S
T
R
W
E
X
C
B
D
F
Y
H
G
A
P
K
L
SECTIONAL ELEVATION
SECTION ON X-Y
SECTIONAL PLAN

Fig 6

Fig 5

Fig 4

Scale about $\frac{1}{7}$th natural size.

carbons were used with a current of 20 ampères. Considerable advantage was gained from the 200-volt supply instead of 100-volt used before. The carbons could be left some ten minutes before it became necessary to feed them up. The lens was an ordinary 4-inch lantern condenser, of Herschel's construction (convex meniscus near the light, combined with double convex). The light was placed in its focus by turning the lantern aside and observing the image on a distant wall. In this way, moreover, it was ascertained that the maximum divergence of the rays was within the permissible limits, three or four degrees from the axis. After leaving the lens, the beam passed through a water cell 2 inches thick, through which a continuous flow of cold water was maintained. It then passed through the outer diaphragm, F, into the apparatus.

The optical train for examining the scattered light is shown diagrammatically in fig. 7, the distances, however, being to scale.

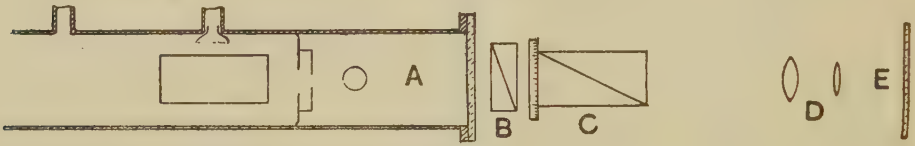

Fig. 7.

Scale about ⅛th natural size.

B is the double image prism placed immediately in front of the window, A. It is of Iceland spar and quartz, the latter being used to secure direct vision for the point midway between the two images. The quartz is cut with its refracting edge parallel to the optic axis, so that no complication arises from the rotatory property. Quartz was used instead of glass, in order to transmit ultra-violet rays and for the same object cement was dispensed with.* No use was eventually made of extreme ultra-violet light, and I regretted that this construction had been adopted, as it gives rise to undesirable reflexions.

C is a Nicol prism of 1¾ inches aperture, very clear and transparent. Its angular position could be read to one-tenth of a degree.

D represents the Dallmeyer kinematograph lens, working at *f*/1·9, the same as was used in the former investigation. E is the photographic plate.

The camera is not here described in detail. It was a special one, arranged for taking a number of exposures on the same plate. The distance through which the plate was moved vertically between exposures could be read on a scale attached.

* The ideal plan is to use spar for both prisms, according to Wollaston's construction. Material could not be obtained for this.

§ 8. *Optical Adjustments.*

The supports of the vessel were adjusted to make it level before the glass windows were put on. A spirit level could be put on the bottom of the parts CB. In the case of the tube AM it was sufficient to level the outside.

The slide on which the positive carbon of the arc was fed up was also levelled, and the beam was brought to the axis of CB, fig. 4, by observing its outline on the windows D and E.

With the green glass horn temporarily removed and a clear view through the tubular part AM, the polarising prisms and the photographic lens were readily adjusted to be in the axis of the tube, which was accurately at right angles to the part BC (fig. 4), which contained the primary beam.

The rectangular aperture L was focussed on the photographic plate. The image was, of course, duplicated by the double image prism, and the latter had to be placed so that the images had their directions of vibration respectively vertical and horizontal.

A preliminary examination of the behaviour of the prism made with the help of an accurately vertical glass plate at the polarising angle and a plumb line, had shown that the directions of vibration in the images were respectively parallel and perpendicular to the line joining them. It was therefore merely necessary to set the prism at such an angle that the line joining the two images was vertical, or, on a photograph, parallel to the edge of the plate, itself vertical during the exposure.

As explained in my former paper, very moderate accuracy in this adjustment is enough. If θ is the angular error, its effect on the intensity ratio depends only on θ^2.

For a similar reason, the line of vision need not be very exactly at right angles to the primary beam. This is fortunate, since considerations of intensity make a slight divergence in the primary beam inevitable.

The actual extreme divergence, three or four degrees from the axis, could do no harm. The same consideration shows that the greatest obliquity to be found in any of the rays collected by the photographic lens is well within the admissible limit.

We come now to one of the most important tests, that of the adequate blackness of the background. Evidently, if the back wall of the apparatus adds anything appreciable to the light scattered by the gas, serious error will be introduced; for the state of polarisation of this added light will not in general be the same as that due to the gas. To check this point, a photograph was taken with the apparatus exhausted to a small fraction of a millimetre of mercury, and the nicol away. Twenty-four hours' exposure was given, extending over three working days. The plate was fully developed, and showed the two images of the rectangular aperture, L, *in outline*, this outline being due to light scattered by the edges of the diaphragm itself. The area inside the outline was in each case perfectly clear to the eye, and examination with the photo-electric apparatus showed no detectable difference between these areas and the clear film outside them.

In determining the intensity ratio corresponding to each position of the nicol in the manner already outlined (p. 438), it was considered undesirable to remove the optical parts from their places in the apparatus. The calibration was carried out *in situ*. It was necessary to back the rectangular diaphragm L with unpolarised light. This was done by taking off the glass horn and placing a diffusing screen of ground glass, combined with several thicknesses of tracing paper over the flange. Immediately behind this was placed a lens of about 12 inches focal length, with a "Pointolite" lamp in the principal focus. The lens was to ensure that the rays fell perpendicularly on the diffusing screen, but was perhaps scarcely needed.

The method of calibration requires diaphragms to reduce the lens aperture. If the ordinary photographic stops were used, it would be necessary to assume that every unit element of area in the full aperture contributed equally to the intensity. It was better to avoid this assumption, and the diaphragms were made in the form of a number of holes of about 1·5 mm. diameter spaced as nearly uniformly as possible over the full aperture. In no case was the number of holes used less than nine, so that a fair average of all parts of the area was secured. The holes were drilled in thin sheet zinc, and lightly countersunk on both sides with a tool held in the fingers, to remove the raggedness of the edges. The necessity for countersinking was regrettable as it slightly affected the diameter, which had therefore to be measured in each case. The diameters of the holes were determined to about 1 per cent. with a travelling microscope.

The "full aperture" used in the calibration process was a circular one turned in the same sheet zinc and measured in the same way. It was very slightly smaller than the full aperture of the lens as used for the actual exposures on scattered light. The latter formed part of the lens mount and was not conveniently accessible for exact measurement. No sensible error can be introduced by this procedure, the calibration merely requiring comparison of *apertures used in calibrating*.

The result of the calibrations was as follows :—

Reading of Nicol for equality.	Area (full aperture = 100).	Intensity, corrected for false light (full aperture = 100).
265 ·50	2 ·32	1 ·64
266 ·76	3 ·24	2 ·56
267 ·84	3 ·98	3 ·30
268 ·78	4 ·84	4 ·16
270 ·4	6 ·34	5 ·66
272 ·19	8 ·22	7 ·54
273 ·28	9 ·68	9 ·20
274 ·29	11 ·0	10 ·3
275 ·47	12 ·6	11 ·9
276 ·50	14 ·5	13 ·8
278 ·20	17 ·4	16 ·7

These values were plotted on a large scale for interpolation, and a smooth curve drawn through them, using a flexible lath. The values lie very well on the curve. Taking the areas as absolutely correct, the curve, as drawn, does not in any case give a position of the nicol differing by more than 0·15° from that experimentally determined. Thus the calibrations appear reasonably concordant, and free from unsystematic error. It is believed that there would not be much advantage in determining more numerous points on the curve or in repeating the determinations already made.

To judge from the evidence of the curve, it would seem that the errors which could be eliminated by doing so, are probably not more than about 3 per cent. on the value of the ratio in the second column. Larger systematic errors may be present, but repetition will do nothing to eliminate them.

§ 9. *Experimental Results.*

In the following Table, the first column of numbers gives the actual angular setting of the nicol required to equalise the images in each case, and the second the intensity of the weak component polarisation, taking the strong one as 100. This second column is obtained by placing the numbers of the first column on the calibration curve.

Gas.	Angle of Nicol degrees.	Intensity of weak component polarisation (strong component = 100).
Hydrogen	268 ·47	3 ·83
Nitrogen	268 ·72	4 ·06
Air	269 ·78	5 ·0
Oxygen	273 ·6	9 ·4
Carbon dioxide	275 ·3	11 ·7
Nitrous oxide	277 ·5	15 ·4

Each angle arrived at is the result of about ten photographs, either side of the position of balance. In the case of air, for example, four photographs were taken at 269·5° and six at 270°.

For the former, the differences of density, in scale divisions of the galvanometer, were +18, +6·4, +12·3, +6. For the latter, −3·0, −4·2, −14·4, −4·0, −13, −10·6.

Each of these exposures lasted two hours in the case of air.*

The numbers given for air well illustrate the degree of concordance obtained from different photographs. It will be noticed that a rotation of the nicol of $\frac{1}{2}$° shows the transition from too low to too high a reading very definitely. It is hoped that the final interpolated value is not more than 0·2° in error. I am confident that hydrogen and nitrogen are really in the order given.

The value of the ratio of intensities given in the second column is, of course, subject to the error of calibration, which may in some cases conspire with the error of setting. I shall be disappointed, however, if future investigation proves the results here given to be in error by much more than 5 per cent.

Note on the Influence of Temperature on the Rigidity of Metals.

By A. Mallock, F.R.S.

(Received June 9, 1920.)

In these 'Proceedings,'† I described some experiments on the influence of temperature on the value of Young's Modulus for various metals. The results showed that the more fusible the metal, the greater was the variation of the modulus with temperature, and suggested that, roughly, the decrement of the modulus for a given rise of temperature was equal to the ratio of the modulus at absolute zero to the melting temperature and a constant (*i.e.* $dM/d\theta = M_0/(\theta_n + \theta')$). Since Young's Modulus is a complex constant, involving both rigidity and volume elasticity, it seemed worth while to examine the temperature effect on rigidity alone, and with this object in view I have recently carried out‡ a further series of experiments on most of the metals previously tested.

The apparatus used was a torsion-balance, shown diagrammatically in fig. 1. A vertical rod, A, is suspended by a long fine wire, B, and the test piece, C, in the form of a wire or narrow strip of plate, is clamped to the lower end of A, and also to the fixed support, D. The whole of this part of the balance can be immersed in a bath of fluid at any required temperature.

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* For hydrogen six hours were necessary to get adequate density.

† A, vol. 95, pp. 429–437.

‡ At the Davy-Faraday Laboratory.

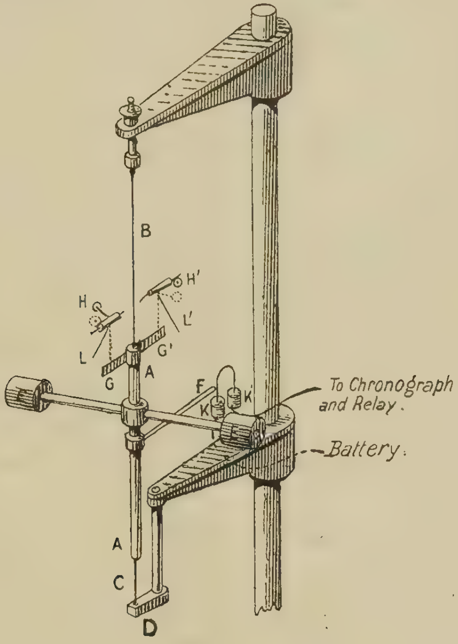

Fig. 1.

A, carries a horizontal loaded arm, E, and also the two light arms, F and G. A U-shaped wire at the end of F makes an electrical contact between drops of mercury in the cups K, K′, as the balance passes its zero position, and by means of an electromagnetic arrangement, not shown in the figure, the two small weights, H, H′, are allowed to drop, and acting through the arms, L, L′, at either end of G, produce a couple tending to accelerate the rotation of A. It is arranged, by means of a relay, that this action should only take place once in each complete oscillation, and not at each passage of the U-shaped wire through the mercury. Each passage, however, is recorded on the chronograph, as by so doing it can be seen whether the maintaining couple is symmetrically applied. The natural period of the balance on the suspension wire, B, is long (about 150 seconds), but with the test piece in position the periods were generally of the order of from 5 to 10 seconds according to the thickness and length of specimen tested.

If T_B is the period of the balance on B,

T_{θ_1} is the period of the balance with the test piece at temperature θ_1,

T_{θ_2} is the period of the balance with the test piece at temperature θ_2, then the ratio of the rigidities of the material tested at θ_1 and θ_2 is

$$n_{\theta_1}/n_{\theta_2}/ = \mathrm{T}_{\theta_1}^2/\mathrm{T}_{\theta_2}^2 \times (\mathrm{T}_{\mathrm{B}}^2 - \mathrm{T}_{\theta_2}^2)/(\mathrm{T}_{\mathrm{B}}^2 - \mathrm{T}_{\theta_1}^2).$$

$(\mathrm{T}_{\mathrm{B}}^2 - \mathrm{T}_{\theta_2}^2)/(\mathrm{T}_{\mathrm{B}}^2 - \mathrm{T}_{\theta_1}^2)$ in practice never differs much from unity. If for example, $\mathrm{T}_{\mathrm{B}} = 150$, $\mathrm{T}_{\theta_1} = 10$, and $\mathrm{T}_{\theta_2} = 9$, its value is about 1·001, so that the correction to $\mathrm{T}_{\theta_1}^2/\mathrm{T}_{\theta_2}^2$ (which would be the value of $n_{\theta_1}/n_{\theta_2}$ were T_{B} infinite) is hardly sensible.

In making a set of experiments the oscillations of the balance were maintained throughout, the only quantity varied being the temperature of the bath in which the test piece was immersed. The conditions thus being identical at all temperatures (except as regards the small expansion or contraction of the test piece, which can be allowed for), it was hoped that correct measures of $n_{\theta_1}/n_{\theta_2}$ would be obtained, and this would have been the case had the rigidity been the only quantity affected by change of temperature.

It was soon found, however, that all the metals had considerable internal viscosity, and that the viscosity was even more affected by temperature than the rigidity. This was particularly noticeable in the pure annealed metals used in these experiments.

The lower the temperature the less the viscosity, and hence the greater the amplitude of the oscillations with a constant maintaining couple: and although in any one set of experiments the periods as measured at each temperature seldom differed from one another by more than two or three parts in ten thousand, any alteration of adjustment gave equally concordant but different values.

It seemed worth while, therefore, to examine in some detail the causes which operated to produce these differences. In the first place, if the motion is resisted by a force proportional to the velocity, the period is dependent on $\sqrt{(n^2 - \kappa^2)}$ (n and κ being the coefficients of rigidity and resistance), and not on n alone. Also, in most, if not all, well-annealed metals, κ is not a constant for a definite temperature, but depends also on the absolute time for which the distortion lasts. This is conspicuous in the case of pure rhodium, platinum, gold, aluminium, and zinc, and the same property may be observed in many non-metallic substances.

A small tuning-fork or bar of hard pitch, for instance, will at ordinary temperatures give a definite note, showing that several vibrations have occurred before the motion is extinguished, but it is only when the vibrations are very rapid that this happens.

Thus, even were it possible to measure with sufficient accuracy the period of a free but rapidly decaying oscillation, the nature and magnitude of κ would have to be known before n could be determined. When, however, κ is large, some form of maintenance is necessary in order that the period may be measured, and, when the maintenance is supplied, as in these experiments, by a constant couple acting for part of each oscillation, its effect on the period may be illustrated by the diagram in fig. 2. Let force and displacement be measured parallel to Y and velocity parallel to X. Also let the free oscillations be about the point O. Then the co-ordinates of the circle of radius OA will represent (x velocity, y restitutive force and displacement) an unresisted oscillation OA $\cos\theta$, where $\theta = 2\pi t/\mathrm{T}$, T being the period.

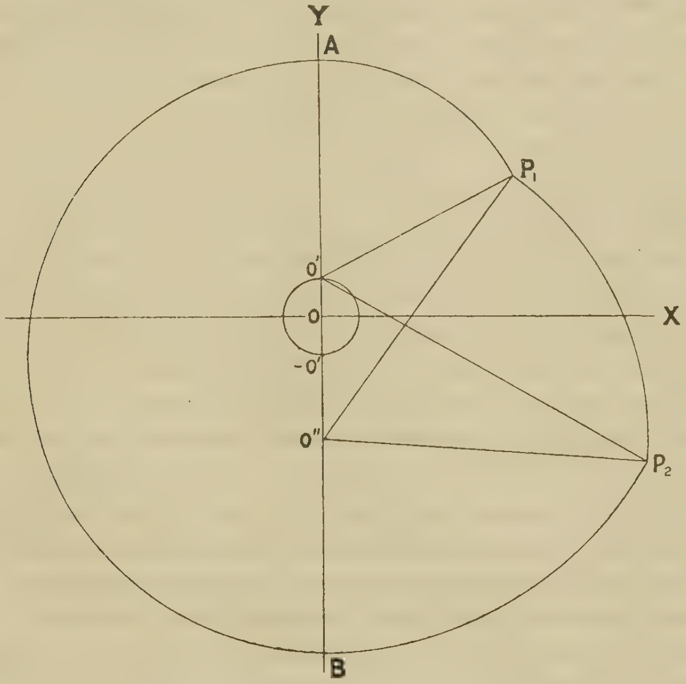

Fig. 2.

Suppose, in the first place, that the motion experiences a constant resistance, OO′, such as would be produced by solid friction. If there is no maintenance, the result is an oscillation, still, with period T, of amplitude OA−OO′, about O′ from $\theta = 0$ to $\theta = \pi$, followed by a similar oscillation of amplitude OA−3OO′, about (−O′)O from $\theta = \pi$ to $\theta = 2\pi$. Thus, an oscillation with initial amplitude, OA, opposed by a constant force measured by OO′, decreases by a constant quantity, 4OO′, at each oscillation, and ceases when amplitude is so far reduced that the path cuts the circle of radius OO′ about O.

At the point P_1 of the circle with radius O′A, let a constant maintaining force, measured by $O'O''$, come into action. The motion will then be represented by a circle of radius $O''P_1$ about O''. There will, of course, be no sudden change of velocity at P_1, but there is a sudden change of virtual amplitude from $O'P_1$ to $O''P_1$, and a change of phase equal to $-O''P_1O'$. Let the circle of radius $O''P_1$ be continued from P_1 to P_2, and there let the maintaining force cease while the resistance continues to operate. The further motion, until dy/dt changes sign at B, is represented by a circle of radius $O'P_2$ about O', and there is a change of phase of $+O'P_2O''$ at P_2. For the last half oscillation, the amplitude is $(-O')B$. If the maintained oscillations are to be repetitions of one another, $(-O')B$ must be equal to $(-O')A$.

The periodic time in each of the parts into which the complete oscillation is thus divided is T, as before said. Hence the total time between successive passages through A is measured by the sum of the angles $AO'P_1+P_1O''P_2+P_2O'B+\pi$. This is equal to 2π when $O'P_2O''-O''P_1O'=0$. That is, the maintained period is unaltered and equal to T when, and only when, the sum of the changes of phase introduced by the maintenance is zero.

If instead of a constant resistance the extinction force is proportional to the velocity the natural period is dependent on $\sqrt{(n^2-\kappa^2)}$, and the circles in fig. 2 must be replaced by appropriate logarithmic spirals, but the above condition for no alteration of period by maintenance still holds.

All the differences found in the present experiments for values which should be identical (differences which though very small compared to the periods themselves were often of the same order as differences due to variation of rigidity) can be traced either to the unknown and varying viscous resistance which depends not only on the chemical purity of the metal, but also on its mechanical condition, on the temperature, and on the absolute period of the balance; or to the effect of maintenance, which if correctly adjusted for phase alteration as regards a certain amplitude ceases to be so when the amplitude varies.

The general conclusions, however, as regards rigidity agree with those previously derived from the experiments on Young's Modulus and show that the more infusible the metal the less is rigidity affected by change of temperature, but I do not regard the numerical results obtained as being sufficiently accurate for publication, although the method by which they were reached and the difficulties met with are worth recording.

A few experiments were made on non-metallic substances, among which indiarubber was included. Sir James Dewar called my attention to the great change which takes place in its rigidity when the temperature is low, and on trial I found that at the temperature of liquid air n was between 800 and 1000 times as great as at 15° C. With ebonite on the other hand the difference was only about 1·5 to 1.

Preparations are being made for a further series of experiments by a method which will record viscous resistance as well as the amplitude and period of the oscillation.

An Extension of the Balmer Series of Hydrogen and Spectroscopic Phenomena of very long Vacuum Tubes.

By R. W. Wood, For. Mem. R.S.

(Received June 21, 1920.)

[Plates 1 and 2.]

The spectrum of hydrogen has probably received more experimental study than that of any other element, and yet in spite of the extended series of lines exhibited by solar hydrogen (a Balmer series of 32 lines), the vacuum tube has steadfastly refused to exhibit more than the first 12 members. The solution of the problem looked rather hopeless at the start, for every possible method of electrical excitation, combined with variable gas pressure, various tube diameters, presence or absence of foreign gases and vapours has been tried over and over again. It will be remembered that by employing absorption as a method of locating the lines, I was able to extend the Balmer series of sodium from the eight members previously known in the emission spectrum, almost indefinitely; 48 in the first investigation, and 56 in a subsequent one made in collaboration with R. Fortrat with the very powerful quartz spectrograph of Prof. Weiss at Zurich,* a further extension being merely a matter of increased resolving power and length of the vapour column. This method is impracticable, however, in the case of hydrogen, since this element shows absorption only when subjected to electrical excitation, which of course introduces the same difficulties which occur in the case of the study of the emission spectrum.

The first thing to determine, in attempting to add more lines to a series, is the factor which has heretofore fixed the limit of the series.

A somewhat careful study of the literature on the subject failed to yield any very definite information regarding this matter. I could not, in fact, find any reproduction of a spectrogram of the series which showed more than the first five or six lines, and could thus form no idea of the conditions at the portion where the higher members failed to record themselves.

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* 'Astrophys. Journal,' 1915.

We have, of course, Bohr's theory that the higher members are absent in vacuum tubes owing to the fact that the molecules are too close together to allow room for the very large orbits necessary to give birth to them.

This at all events suggests a method of attack: work at very low pressures and employ very long end-on tubes to give the necessary amount of light. In the case of the end-on capillary tubes as commonly employed, it is doubtful if much light from the remoter parts of the tube reaches the spectroscope. To have every element of length contribute an equal amount of light (neglecting possible absorption by the luminous gas) the following conditions must be fulfilled. The bore must be large enough to permit of the propagation of light according to the laws of geometrical optics, in other words we should be able to see a luminous object distinctly through the tube. The tube should be placed at a considerable distance from the slit of the spectroscope, so that its two ends subtend substantially the same angle as seen from the slit. The aperture of the lens which projects the image on the slit should be restricted to a diameter such that it passes equal quantities of light from the two ends of the tube. This last condition perhaps is not very important owing to internal reflections in the tube, without which the light from the further end of a very long tube will issue in the form of a very narrow pencil of rays, whereas the light from the near end will fill a large cone.

My first tube had a length of about 1·5 metres and was placed at a distance of 3 metres from the spectroscope. Its bore was about 5 mm., and was bent at a right angle near each electrode bulb, the angle of the bend being blown out into a bulb of very thin glass. Clear vision was possible through the tube. To make sure that it was accurately aimed along the axis of the collimator the following expedient was used. A small tungsten lamp with a concentrated filament (motor lamp) was mounted in front of the centre of the collimating lens and the slit opened ½ mm. The diameter of the beam, passed out by the slit, at a distance of 3 metres was about 5 mm. and the tube was mounted in such a position that the rays passed directly down it, the strongly illuminated slit being visible when the eye was brought up close to the bulb.

Though the original plan of working at very low pressures proved to be the wrong line of attack, at least under the present conditions, the experiment led to the discovery of a most remarkable type of tube and a wholly new set of spectroscopic vacuum-tube phenomena. It is probable that a quite new field is opened up for the separation and study of compound spectra. It appeared very early in the experimental work that the obstacle to the extension of the Balmer series was the faint continuous spectrum, and to a lesser degree the secondary spectrum. In an ordinary vacuum tube the 12th line is so faint that one must know exactly where to look for it, in order to locate it among the numerous lines of the secondary spectrum. Prolonged exposure brings out no new lines on account of the continuous background, which is stronger than the lines sought. Reducing the pressure only makes matters worse, for the intensity of the continuous background increases enormously as soon as the Crookes' dark space exceeds 12 or 15 mm. in thickness. The decrease in the intensity of the lines of the series, combined with the inevitable presence of a continuous background, is evidently what has placed the limit heretofore.

By means of methods to be presently described the series has been photographed down to the 20th line, the intensity of which is probably less than one-millionth that of H_α with an exposure of only half an hour in the third order spectrum. True the series has been increased by only eight lines, but when we consider that the 20th line has an intensity of about 1/250 of that of the 12th line (the previous limit) the advance is seen to be no small one. It has been accomplished by devising a method of practically abolishing the secondary spectrum and the continuous background, or to be more exact, of reducing it to about 1/40 of the intensity (relative to the Balmer lines) which it has in an ordinary tube.

The discovery of the new type of vacuum tube resulted from the observation that the central portion of the long tube previously described, when viewed through a direct vision prism, showed only the Balmer lines with no trace of the secondary spectrum. The form of tube finally adopted is shown in fig. 1. Its length is about 2 metres, and the bore 7 mm.

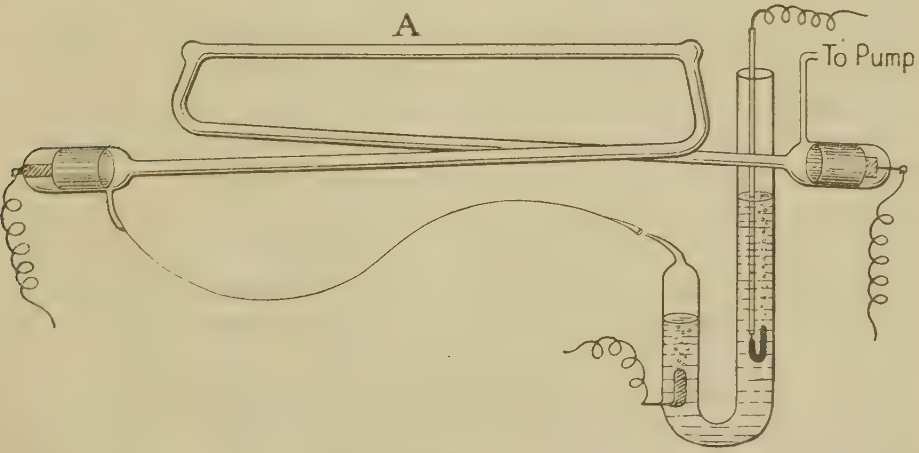

Fig. 1.

The straight portion A is used end-on, and all of the phenomena described in this paper occur only in this portion of the tube, unless specific reference is made to the curved branches. The precise form of the tube is immaterial: it is bent as figured merely to take up less room. The essential thing is to have an end-on portion about 40 cm. in length, separated from each electrode bulb by at least 80 cm. of tubing. One end of the tube is in permanent connection with a Gaede pump, which is usually in continuous operation, while hydrogen is fed continuously into the other end, either moist, from an electrolytic generator, through a long and very fine capillary tube, or dry, through a palladium tube heated in a small flame of hydrogen. The electrodes are cylinders of sheet aluminium, about the thickness of writing paper, and completely fill the glass cylindrical end-bulbs. This type of electrode, being supported by the glass walls, can be very easily inserted, as the sealing-in wire does not have to support the weight of the electrode. The copper plated alloy wire used in lamp manufacture answers admirably.

The tube is operated by the current from a small transformer, giving a potential of about 25,000 volts. Its primary is fed with a 60 cycle A.C., as much as 30 ampères being used on some occasions. Currents as large as 0·2 of an ampère can be carried by the tube with safety, if the hydrogen is at the right pressure.

The appearance of the tube is most remarkable, the colour of the discharge being bluish white to a distance of perhaps 50 cm. from each bulb, while the straight central portion is of a fiery purple, of an intensity which is almost painful to the eyes. If we view the tube through a prism (preferably a large direct vision one) we find that the central portion shows only the Balmer lines, of which four are in the visible spectrum.

The region between the lines is quite black in appearance, and I shall speak of the tube in this condition as in the "black stage." A photograph of a portion of the tube taken through a prism is reproduced, fig. 1, Plate 2.

Viewed through a green colour screen, which cuts off completely the light of the Balmer lines, the tube appears illuminated with a feeble light, which shows that there is a trace of the secondary spectrum left. I have never quite succeeded in abolishing it entirely, though I have, on occasions reduced it to such an extraordinary feebleness, that I have a notion that if the pressure, current intensity and rate of flow of the gas, together with the amount of water vapour present were in very exact adjustment, the secondary spectrum might vanish altogether. The lateral branches of the tube show the secondary spectrum in addition to the Balmer lines, and it is not until we get to a distance of about 50 cm. from the electrode bulbs that it begins to vanish. It will be a matter of considerable interest to investigate the electrical conditions within the tube, for I imagine that the potential gradient will show marked variations.

This "fractionation" of the compound spectrum into different parts of the tube constitutes one of the many new phenomena exhibited by these very long vacuum tubes, and it is this separation which has made possible an extension of the Balmer series. I shall describe later on how it is possible to abolish completely the Balmer lines and have only the secondary spectrum in the central part of the tube.

It requiries some practice in developing the technique of operating the tube before the secondary spectrum can be reduced to the point at which it is no longer visible with the direct vision prism. I have never reduced its intensity to zero, but have obtained a measured intensity of about 1/40 of that shown in the lateral branches of the tube.

The direct vision prism is in constant use during the operation of the tube, and it is well to have in addition a dark green ray filter, absolutely opaque to the light of H_α, H_β, and H_γ.

Through this screen we see the tube only by the light of the secondary spectrum, and can form a better estimate of how nearly we have abolished it. The size and length of the capillary must be so chosen that, with the pump in operation, the depth of the Crookes' dark space is about 6 mm. It is well to have the cylindrical electrodes joined to the sealing-in wire by a narrow strip of aluminium, as shown in fig. 1, for the observation of the dark space, as it cannot be seen to advantage within the electrodes.

The electrolytic hydrogen generator is of the form shown in fig. 1, the electrolyte being a solution of phosphorus pentoxide. It can be left in permanent connection with the battery, as the circuit is automatically broken as soon as the tube is filled with hydrogen. The upper end of the tube is drawn out into a capillary of sufficiently small bore to prevent any considerable escape of the gas during the process of changing the long capillary thread which conveys the gas to the discharge tube. This thread terminates in a short section of tubing with a bore of 2 mm. which is slipped over the generator capillary and sealed with sealing-wax. The other end is then inserted into the discharge tube and sealed in the same way. For the experiments with pure dry hydrogen, I substituted an old X-ray bulb provided with a palladium tube, for the electrolytic generator. The end of the metal tube is heated with a very minute hydrogen flame burning at the tip of a glass capillary.

In constructing the tube care should be taken to avoid having any portion in close proximity with any other portion, as if this is the case the tube is sure to be punctured, owing to the potential difference between the adjacent surfaces.

We will now take up the subject of the extension of the Balmer series, and later on a discussion of some very remarkable spectroscopic phenomena exhibited by this type of tube.

Extension of the Balmer Series.

With the tube in the best condition to which I have been able to bring it, 20 lines of the series have recorded themselves on the plate. Unless the pressure is exactly right, it is difficult to get anything below the 16th. This pressure is such as to give a Crookes' dark space of about 6 mm. If the pressure is gradually raised, the higher members disappear in succession, as they should on Bohr's theory. If the pressure is lowered, they also disappear, though in this case their disappearance seems to be due to a development of a continuous spectrum and the enhancement of the secondary spectrum. There is no doubt whatever regarding the identity of the lines as far down as the 16th member of the series. The identity of the lower members was established by comparison of the plate with one made under conditions giving a strong secondary spectrum and a weak Balmer series. It is possible to bring the tube to what I call the black stage (very weak secondary spectrum) and still fail to secure the higher members. This occurs with a dark space of about 2 mm. The series from the 10th to the 20th member is shown with the iron comparison spectrum by fig. 1, Plate 1, and the series from the 7th to the 14th with the iron spectrum in coincidence by fig. 2. These were taken in the third order spectrum of a large plane grating with a Cook portrait objective of about 1 metre focus. Fig. 3, Plate 1, reproduced as a positive, was made for intensity comparisons and shows the series from the 5th to the 14th line. The strong lines show ghosts, and the oxygen line near H_5 as well as the cyanogen band appear.

Hydrogen.	Wood.	Dyson. (Solar hydrogen.)
12	3722·12	3722·05
13	3712·22	3712·12
14	3703·92	3704·0
15	3697·35	3697·29
16	3691·72	3691·70
17	3686·99	3687·0
18	3682·96	3682·90
19	3679·46	3679·50
20	3676·44	3676·54

The wave-lengths of the higher members are given in the previous table, with Dyson's values for solar hydrogen for comparison. No attempt was made to get them of a very high degree of accuracy, and they are computed with reference to Rowland's standards of iron, as Dyson's were presumably referred to that scale. Next year they will be more accurately determined with a spectrograph of 20-foot focus, possibly to the fifth order spectrum. These values are certainly correct to 0·1, and possibly to 0·05 of an Ångström.

Impurity Lines.

The following impurity lines have been noticed and identified :—

On the short λ side of H_5 Oxygen 3947.

On the short λ side of H_6 Cyanogen band.

On the short λ side of H_7 Oxygen triplet 3830–3825, *never found.*

On the short λ side of H_{10} Oxygen 3749·5.

On one plate three lines between H_{11} and H_{12} one probably Oxygen 3737·5.

On long λ side of H_{13} Oxygen 3712·9.

On long λ side of H_{14} (*very close*) Hg. 3704.

On long λ side of H_{16} Oxygen 3692.

Other lines are secondary spectrum or mercury.

The study of these lines with the tube in different conditions (pink stage, white stage, secondary flash, etc.) is valuable in formulating a theory of the phenomena.

The Intensity Decrement of the Balmer Series.

Comparison of a number of spectrograms taken with widely different times of exposure showed that in the region between the 6th line and the 14th line each line was very nearly twice as bright as its neighbour on the short wave-length side. To test this a little more exactly, a record was then made of ten exposures in coincidence, each exposure being one-half that of its predecessor—15 minutes, 8 minutes, etc., down to 1·7 seconds. If the law of half intensity held, the lines would be of equal intensities in the diagonal rows, one of which is indicated by a black line on fig. 3, Plate 1. This was found to be the case, as nearly as could be judged by simple inspection of the plate. This means that the 14th line has an intensity of 1/256 of that of the 6th line. At the same rate of decrease, the value for the 20th line will be 1/15,000. It seems, however, that the rate of decrease becomes less, the last three lines before the 20th being of not very different intensity.

Between the 6th line and H_α the rate of change is greater (about 2·3), the 6th line having an intensity of, roughly, 1/60 that of H_α. Calling the 20th line 1/10,000 of the intensity of the 6th, we find that it has an intensity of something like 1/600,000 that of H_α. Notwithstanding this, it can be photographed with the long end-on tube in the third order spectrum in

30 minutes without any difficulty. Merton's value of the 4th line for hydrogen and water vapour (1/100 of H_α) would give an even lower value for intensity of the 20th line (about 1/4,000,000 of H_α). Under the present conditions, however, the rate of decrease between H_β and the 6th line was found to be about 2·3. In the case of the nebulæ the decrement appears to be much less, the intensity of the 14th line being 2, while that of the 2nd line is only 100.*

Spectrum Phenomena of the Long Tube.

1. *Transfer of Energy from the Secondary to Primary Spectrum.*—Mention has already been made of the fact that only the Balmer series appears in the middle of the tube when the proper condition of the tube is established. A new tube has to be operated for some time before this happens. At first there is considerable secondary spectrum, but it gradually grows weaker, and finally becomes invisible, except when the green screen is employed. This condition I have called the "black" stage. It occurs only with a fairly heavy current. If we put a lamp bank in circuit with the primary of the transformer and turn on one lamp, a very faint discharge occurs, and the secondary spectrum is as strong as, or stronger than, the Balmer series, even in the centre of the tube. If, now, we add another lamp, both spectra brighten, but presently we shall find that the addition of a new lamp (*i.e.*, increase of current in the tube) causes the Balmer lines to *increase* in intensity and the secondary spectrum to *decrease*. If we look at the tube through the green screen, it becomes much darker when the current is increased, a somewhat surprising effect: a lamp which becomes darker when more current is thrown into it! Of course, what really happens is that the Balmer series becomes brighter each time the secondary spectrum is decreased in intensity by the increase of current.

After a certain stage is reached, further increase of current brightens the Balmer lines, but no further reduction of intensity occurs in the secondary spectrum, which remains at a minimum value, or brightens slightly with each enormous increment of intensity of the Balmer lines.

I am of the opinion that it may eventually be possible, by a very precise adjustment of the condition, to reduce the secondary spectrum to zero intensity. If this can be done, photography of the complete Balmer series will be a question only of resolving power and duration of exposure. Experiments along these lines are in progress. The cause of this transfer of energy from one spectrum to the other will be discussed presently, after we have examined some of the other effects observed.

2. *Secondary-spectrum "Flash."*—This is an extremely interesting and

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* 'Lick Obs. Report,' 1920.

curious phenomenon. If we bring the tube to the stage at which the secondary spectrum has its minimum value, by gradually increasing the current, and then open the primary switch, we find that, if we view the central portion of the tube through the green screen and close the switch, there is a bright flash which lasts for perhaps 1/10 of a second, followed by a steady glow of much diminished intensity, which is the permanent minimum value. This can be repeated as rapidly as we can open and close the switch. If we do this very rapidly, the tube is much brighter than if the switch is kept permanently closed, *i.e.*, the integrated intensities of the light of the discharge produced by *short intermittent currents*, is actually greater than the continuous intensity produced by a *steady current of the same value.* (The current is alternating in both cases, of course.) This is true only for the light of the secondary spectrum, and the phenomenon does not occur if the pressure of the hydrogen is too high. The Crookes' dark space should be 4 mm. or 5 mm. in depth. The phenomenon is best seen when moist hydrogen is delivered to the tube directly through the fine capillary. The hydrogen probably is far from saturated with water vapour, however, after traversing the fine tube. With dry hydrogen, obtained with a palladium tube, the phenomenon is absent after all water vapour has been driven out of the glass by long operation of the tube.

The Balmer lines appear to be of low intensity at the moment when the switch is closed, but rise to their full intensity while the secondary flash is subsiding. This phenomenon is less easy to observe, as an initial dim stage of very brief duration, followed by a bright steady state, is less conspicuous to the eye than an initial bright flash followed by a dim stage. The effect was best seen with a rotating mirror and red glass screen. The first three or four discharges of the 60 cycle A.C. were less bright than those following. The recovery of the condition necessary to produce the flash is very rapid, perhaps 1/4 of a second. A very short interruption of the current (say, 1/20 sec.) does not, however, renew the flash, the tube remaining dim after the interruption. This effect can be studied by including in the primary circuit a U-shaped strip of metal, and a wire which presses against the inside of the U. By striking the wire over to the other side with the fingers, a very short break can be effected.

The water-vapour band comes out very strongly in photographs taken with the quartz spectrograph (fig. 4, Plate 2). It appears to be relatively stronger with a continuous current than with the short intermittent exposures. This was judged from two spectrograms, one built up by 300 short "flashes" and the other with the switch closed throughout the exposure, the total time of operation of the current being about the same in each case.

The "flash" phenomenon was also looked for in the water band, by means of a screen of barium-platino-cyanide in the focal plane of the quartz spectrograph. It was found to behave in the same way as the Balmer lines, that is, it did not flash bright on closing the switch and then fade away, as does the secondary spectrum.

3. "*Infected*" *Spots on Tube Wall.*—It will be found that certain portions of the tube, far removed from the electrode bulbs, sometimes show the secondary spectrum at the full intensity which it has at the ends of the tube. These spots often form at the sharp angles of the tube. When once formed, they are quite persistent. I have called them "infected" spots, as the phenomenon is evidently associated in some way with the condition of the inner wall of the tube, probably the presence or absence of some adsorbed material. They are sometimes very difficult to get rid of, persisting for days; though I find that by allowing air to enter the tube, and re-exhausting, they frequently disappear entirely. Heating the tube almost to the softening point appears to be without influence either in causing or abolishing these spots. There seems to be another type of infected spot which shows the D lines of sodium. These always appear if the tube is heated to a high temperature. Sometimes a spot only 2 or 3 cm. in length will appear in the straight portion of the tube which shows the yellow light. With the direct vision prism we can at once recognise such a spot, as we see a sharply defined yellow image of the tube in the more or less hazy secondary spectrum. If the discharge is stopped and the tube allowed to cool off, the appearance is normal on renewing the discharge, but the yellow spot develops in a few minutes in exactly the same place. Frequently, pink and white spots alternate along a considerable portion of the tube, the secondary spectrum being weak in the former and strong in the latter. The reverse holds for the Balmer lines.

The appearance is similar to what I have frequently observed in Claude's neon lamps, which were to be generally observed in Paris during the winter before the war, glass tubes 20 or 30 feet long, containing neon and mercury. Small portions of the tube often exhibited only the mercury spectrum, though the greater part glowed with the brilliant orange red of neon. I believe that these tubes were furnished with mercury electrodes, and the local patches of blue colour are evidently regions where the mercury vapour is in excess of the neon. These spots often moved about in a curious manner, fading away and then appearing at another point. There may be something of the same kind going on in the hydrogen tube, though I do not feel certain that the cases are analogous. Certain spots in the tube sometimes show almost no trace of the Balmer lines. H_α faint and

H_β barely discernible. At these spots the secondary spectrum has great brilliancy. Close to the electrode bulbs, where the discharge is strongly stratified, the Balmer lines fade away rapidly. No trace of H_α or H_β can be seen in the first stratum, H_α is barely visible in the second, and both can usually be seen in the third or fourth. It will be remembered that Fulcher found that the low potential discharge (hot cathode) in hydrogen showed the secondary spectrum very strong and the Balmer lines weak.

4. *Change of Spectrum after Prolonged Operation.*—We have already discussed the remarkable change which occurs in perhaps 1/10 second, which has been termed the "secondary flash." There is another change, which occurs with a heavy current, after an operation of perhaps half a minute. At the start we have the "black stage," *i.e.*, no secondary spectrum visible, between H_α and H_β. In about 15 seconds a trace of the secondary spectrum appears, and it becomes quite marked after a minute's operation. If, now, the switch is opened, and the tube allowed to rest for two or three minutes, the black stage is found again on closing the switch. This is the *reverse* of the flash phenomenon, and the recovery is slow, whereas, in the case of the flash, the recovery is very rapid. It is my opinion that the rapid recovery of the flash condition is connected with a change occurring in the whole mass of the gas in the tube, whereas the other phenomenon, with the slow recovery, is associated in some way with adsorption of ionised hydrogen or water vapour by the wall of the tube. Langmuir* found that the ionised (atomic) hydrogen given off from a tungsten filament was powerfully adsorbed by the wall of the tube, but that, on heating the wall, it was liberated as molecular hydrogen.

5. *Suppression of the Balmer Series. The White Stage.*—The effects described in the four preceding sections are observed with hydrogen containing water vapour. Passing the hydrogen over, phosphorus pentoxide did not appear to have much influence on the general appearance of the tube, though the "secondary flash" was not as conspicuous as before.

On substituting a palladium tube for the electrolytic generator, no very marked effect occurred on the first day, but, towards the end of the second day, after the tube had been in operation for almost ten hours, a sudden change occurred. During the two days' work, the tube had repeatedly been exhausted and recharged with hydrogen from the palladium tube. Between the tube and the pump was a trap immersed in liquid air, to prevent the diffusion of mercury vapour and vapour from the stop-cock grease, since there appeared to be some reason to suspect that these vapours were influencing the results.

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* Langmuir, "The Dissociation of Hydrogen into Atoms," 'Journ. Amer. Chem. Soc.,' August, 1914.

Numerous spectrograms were taken during the two days, without anything peculiar being noted, except the gradual disappearance of the great water band, when suddenly a very remarkable thing happened. On closing the switch, the central portion of the tube was fiery purple as usual, with little or no secondary spectrum; in about ten seconds it became a whitish pink, and presently bluish white, the direct vision prism showing that practically all of the light now came from the secondary spectrum. After the current had been passing for about two minutes, however, the pink colour returned, the secondary spectrum faded away, and the Balmer series rose again to its usual brilliancy. The electrical current was now stopped, the pump put in operation and the tube exhausted until the bulbs showed green fluorescence on momentarily closing the switch. (If the switch is closed for more than a few seconds with the tube in this stage the bulbs are invariably either punctured, as by a spark, or a small spot is fused and blown in by atmospheric pressure, the bulb appearing as if pushed through with a needle.)

Fresh hydrogen was now admitted as usual, by heating the palladium tube in a minute hydrogen flame for 30 seconds. This time, however, the white stage did *not* appear. After a number of exhaustions and refillings it suddenly came again, and I found, after a number of trials, that while, as a rule, the purple colour is present on closing the switch, if the discharge is stopped as soon as the white stage is at its best (*i.e.*, Balmer lines at minimum intensity) and the tube re-exhausted and then refilled with fresh hydrogen, *the white stage always appears the moment the switch is closed.* If, however, the discharge is continued until the purple stage sets in, and is then stopped, on exhausting and re-charging the tube, the *purple* stage always appears on closing the switch and persists for 5 or 10 seconds, gradually passing over into the white stage, and then again into the purple stage. I have sometimes succeeded in getting the tube into such a condition that the white stage persisted indefinitely with continued operation.

The white stage is produced at its best only after being repeatedly produced. It may require an hour or two of work. Then H_β is practically invisible in the direct vision prism, and there is only a faint trace of H_α. The fading away of H_β is an interesting phenomenon to watch. It usually weakens first at the ends of the straight central portion of the tube, the weakening pushing in towards the centre from the ends, until finally the line fades away entirely. This is the moment at which the current must be stopped, and the tube re-exhausted and re-filled, to get the best condition for the appearance of the white stage on closing the switch. I did not succeed in completely abolishing H_α, though I put the tube through this cycle of operations for an entire day. Possibly, if it were persisted in for a longer time, H_α would finally go. Apparently, the production of the Balmer series requires a trace of water vapour. The long operation of the tube, with repeated exhaustions and re-chargings with dry hydrogen, finally removes the water occluded by the glass, and we then get the secondary spectrum only.

Continued operation at the white stage may eventually liberate more water vapour from the glass, and the purple stage then reappears. The difficult question is: "Why do we have the purple stage on closing the switch, followed in a few seconds by the white stage?" The clue to the answer is evidently to be found by considering the peculiar difference in the initial condition (at the closing of the switch) *according to whether we* stop the discharge (and re-fill the tube) at the white stage or at the purple stage. Since what we introduce into the tube is the same in each case, the difference must be in the condition in which we leave the wall of the tube. If the Balmer lines (which give the pink colour) depend upon the presence of water vapour we must conclude that the vapour is liberated from the surface of the glass the moment the current is started. This gives the pink stage. To account for the white stage which immediately follows, we must assume that the water vapour disappears; just how this happens is not easy to say. It may be dissociated and the ions driven away from this portion of the tube, but the fact that the Balmer lines fade away first at the *ends* of the straight central portion of the tube seems to be against this view. The subsequent re-appearance of the purple stage can be explained by the heating of tube by the prolonged operation, more water being driven to the inner surface and liberated. If we stop the discharge at the white stage (in which condition the inner *surface* of the tube is free from water), and allow the tube to cool off, exhaust and re-fill, we get the white stage at once on closing the switch, as the inner surface of the tube is still free from water.

Difficulty is sometimes found in bringing the tube to the white stage. That we are approaching the condition is indicated by the appearance of the green and yellow mercury lines half a minute or so after closing the switch. The best plan to follow is to operate the tube for several hours on the heaviest current which it will bear, say 2 ampères, exhausting and recharging every ten minutes or so. The current must be stopped as soon as the discharge shows signs of "flickering" in the bulbs (which occurs just before the cathode ray fluorescence appears), otherwise the bulbs will be punctured. Then reduce the current to 0·05 ampère and stop the discharge each time at the moment when the secondary spectrum attains its maximum intensity which will occur in half a minute or so after closing the switch. Then exhaust and re-charge, repeating the above-described operation. Each time it will usually be found that the Hg lines and the secondary spectrum will become stronger, and presently the white stage will appear. It requires some patience to coax the tube into this condition, but the phenomenon is very striking when it finally occurs.

Spectra showing the gradual transition from the time of first starting the tube to the white stage are reproduced on fig. 4, Plate 2. H_β is the line at the extreme right, and the lower spectrum was taken first, with the tube containing some air (nitrogen bands show). The ammonia lines also appear on this plate.

The transitions from the pink to the white stage and back were studied with a small quartz spectrograph, which required an exposure of but a few seconds and was well adapted to catch the transient stages of short duration. On looking over these plates I found that all spectra of the white stage showed, in addition to the secondary spectrum, a pair of lines between H_3 and H_4. I have indicated them by two arrows on fig. 3, Plate 2. The lower spectrum shows scarcely a trace of them; this was made when the white stage was less perfectly developed, H_2 being still visible to the eye. On photographs made of the secondary spectrum under ordinary conditions (hydrogen with a trace of water vapour and small current) there is absolutely no trace of them. On another occasion, when the tube had a very minute leak, sufficient only to give a dark space of 3 mm. after standing highly exhausted over night, I found that when the white stage developed, the spectrum showed chiefly the nitrogen bands. A similar phenomenon was found with helium. On closing the switch the line spectrum was all that could be seen, and the tube was bright yellow; but after a minute or two, a brilliant white patch developed, which showed the nitrogen bands.

When the tube had been brought to a point very near the "white stage" and the Balmer lines were comparatively weak, a small amount of oxygen was admitted to the tube, and photographs made every five seconds with the quartz spectrograph. The addition of the oxygen caused the Balmer lines to brighten and the secondary spectrum to diminish in intensity. No trace of the water band was visible in the first exposure, but it appeared after one minute's operation of the tube. The tube was then highly exhausted and fresh hydrogen admitted through the palladium tube. The Balmer lines were bright and the secondary spectrum very weak; there was no trace of the water band during the first five seconds but it developed after a run of one minute. These experiments make it appear as if the water vapour was adsorbed by the wall as rapidly as it formed, and was then liberated again as the temperature of the tube rose. This is a matter, however, which requires further investigation. The appearance or no appearance of the oxygen line near hydrogen line No. 5 should be noted in this connection.

These points will be investigated in the near future.

6. *Spectra of Stratifications.*—At pressures at which the tube is usually operated, stratifications appear only in the vicinity of the electrode bulbs. In some cases, when the discharge passed into the white stage described in the previous section, stratifications suddenly filled the entire bulb, though no change had been made in the pressure or potential.

It is possible to have the stratifications appear in the secondary spectrum and not in the Balmer lines: this condition is best obtained by blowing a small bulb in the straight central part of the tube. The bulb acts as a sort of secondary electrode and stratifications develop on both sides of it. Under certain conditions of pressure and potential it was found that (when the tube was viewed through the prism) the secondary spectrum showed the stratifications while the Balmer lines did not. This seems to establish, beyond any doubt, that the spectra are emitted by different entities, for which other evidence exists. A photograph made of the tube and bulb when in this condition, made with the direct vision prism, is produced on fig. 2, Plate 2. It shows strong stratifications in the secondary spectrum, no trace of them in H_α or H_β, a faint trace in H_γ, and increasing traces as we pass to higher members of the series. This apparently proves that the lines of the Balmer series are emitted by different entities, since the discharge may be seen strongly stratified in the 5th line, while no trace of the strata appears in the 1st.

These facts were very carefully studied visually, the intensity of H_α and H_β being reduced by neutral grey absorbing films, but no trace of the strata was found, though the higher members showed them clearly in the photographs. Faint traces of stratification may be easily lost in a photograph through over-exposure. Another photograph, made on an isochromatic plate, which was very insensitive to H_α, showed well the complete absence of any trace of discontinuity.

The strata near the electrode bulbs are sharply defined. They all radiate the secondary spectrum strongly, but no trace of the Balmer lines appears in the first stratum which emits the secondary spectrum alone, a trace of H_α appears in the second stratum, H_α and H_β appear in the third, while further along the series appears in considerable intensity. No difference in the *spacing* of the strata for the two spectra has been observed, which appears to be of importance.

It is also worthy of remark that very often when the tube passes from the pink to the white stage, the entire bulb suddenly fills with stratifications, though no change in the current or the pressure has occurred.

A general discussion of the results recorded in this paper will be more profitable after further investigations have been made. In the autumn I plan to immerse the central portion of the tube in liquid air, which I expect may give the white stage at once. It is also of importance to identify the two lines which appear when the white stage sets in, between the 3rd and 4th hydrogen lines. I made an effort to do this during the last few days before closing my laboratory for the summer, employing the grating instead of the quartz spectrograph, but the tube developed a microscopic leak, and when the white stage finally appeared it showed only the nitrogen bands.

It appears to be well established that pure dry hydrogen gives only the secondary spectrum at any great intensity, and that, for the strong development of the Balmer lines, a trace of water vapour is required. It was found that the same thing could be accomplished with oxygen. Experiments have also been made with helium and with oxygen in the long tube, but the results are still incomplete. In the case of oxygen a curious phenomenon was observed at one stage of pressure, the colour of the discharge changing suddenly, and the soft glass tube phosphorescing with a ruby-red light. I suspect that this red phosphorescence is due to extremely short wave-lengths, which suddenly develop.

Fig. 1

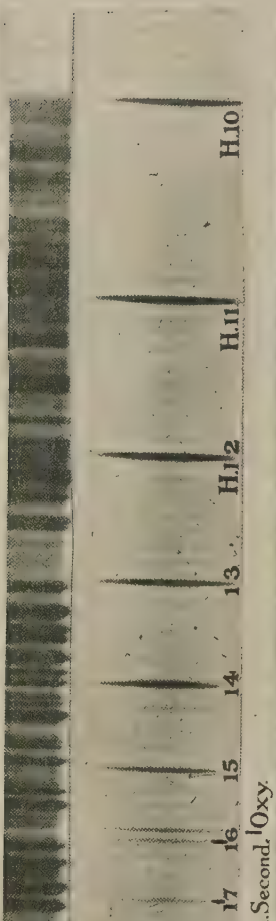

Hg.
Hg.
Hg.
Hg.
Hyd.
Second
20
19
18
Hyd. Second.
17
16
Oxy.
15
14
13
H.12
H.11
H.10

Fig. 2

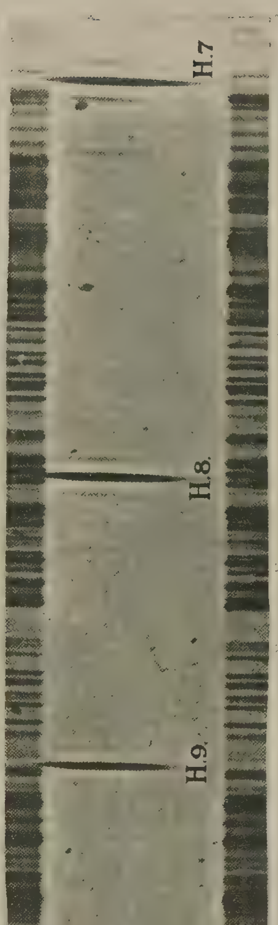
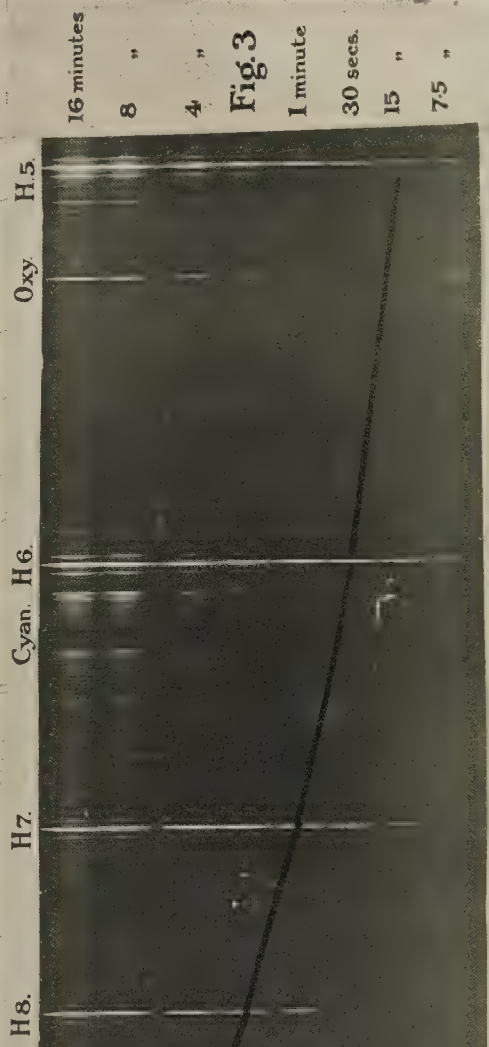

H.13.
H.12.
H.11.
H.10.
H.9.
H.8.
H.7

Fig. 3


16 minutes
8 "
4 "
1 minute
30 secs.
15 "
7.5 "
15
14
13
H.12
H.11
H.10.
H.9.
H.8.
H.7.
Cyan.
H.6.
Oxy.
H.5.

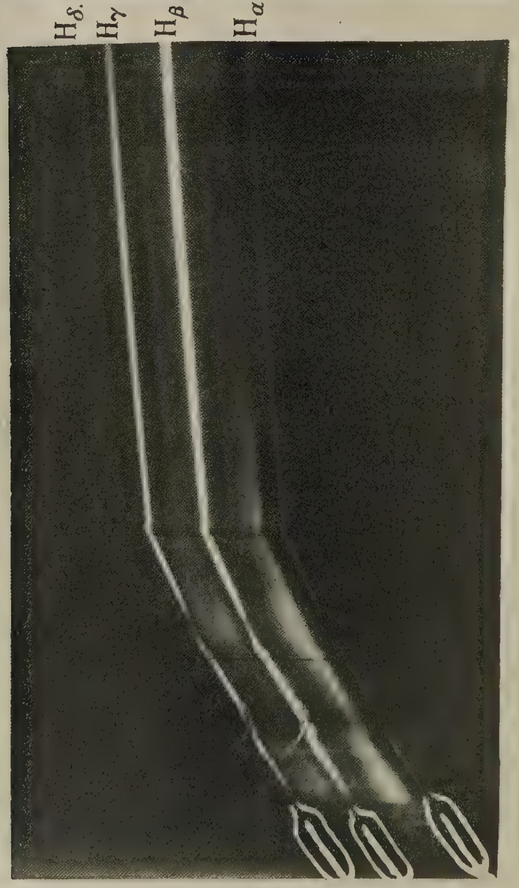


Fig 1

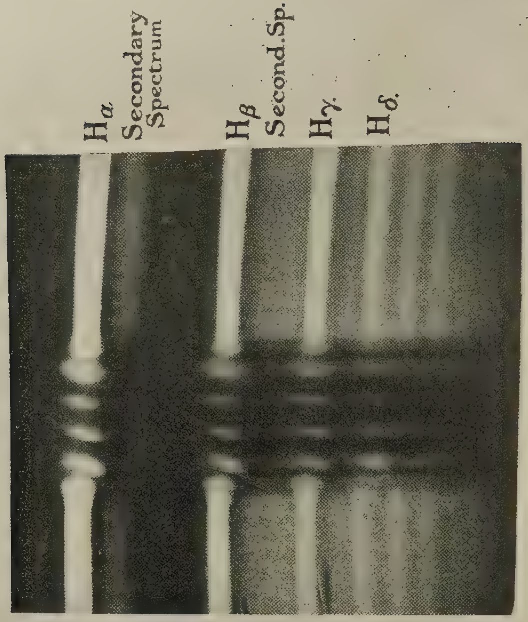

Hα
Secondary Spectrum
Hβ
Second. Sp.
Hγ.
Hδ.

Fig 2

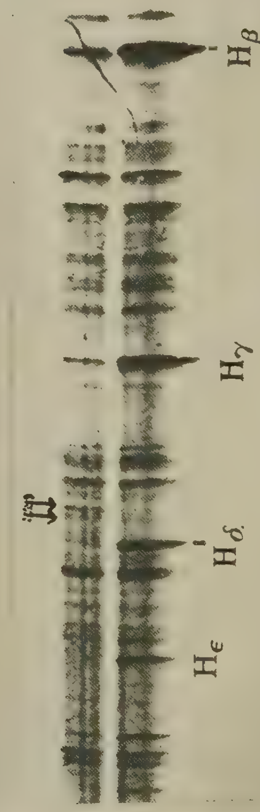


Fig 3

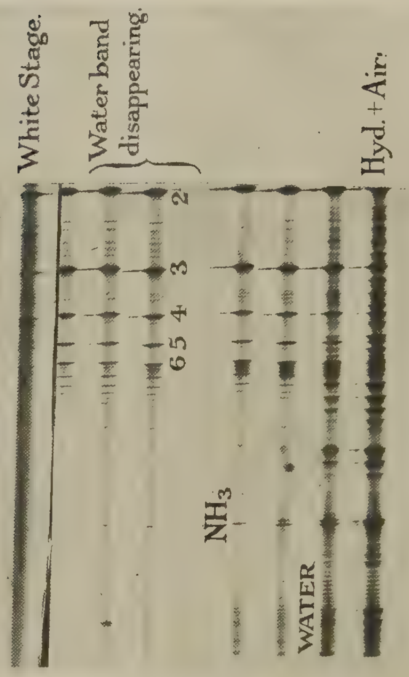

White Stage.
Water band disappearing.
Hyd. + Air.
2
3
4
6 5
NH₃
WATER

Fig 4

OBITUARY NOTICES

OF

FELLOWS DECEASED.

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WILLIAM WATSON, 1868-1919.

Lt.-Col. William Watson, C.M.G., D.Sc., A.R.C.S., Professor of Physics at the Imperial College of Science, London, Director of the Central Laboratory of the British Expeditionary Force in France, from its foundation in 1915 to the end of the war, died in hospital from the results of gas-poisoning on March 3, 1919.

Watson was born in 1868, and educated at King's College School. He received his training in the accurate and delicate physical manipulation which distinguished all his work, at the Royal College of Science under Sir Arthur Rücker and Prof. C. V. Boys, and took his B.Sc. degree in 1890, securing first place on the list of honours in physics. He obtained an immediate appointment as Demonstrator in the Physics Department of the Royal College of Science, and afterwards succeeded to the Assistant Professorship of Physics in 1897. He was elected a Fellow of the Royal Society in 1901, and became in due course one of the Professors of Physics at the Imperial College of Science.

His first scientific work was as assistant in the great magnetic survey of the British Isles under the direction of Profs. Rücker and Thorpe, 1890–95, in which he did the lion's share of the observations, and appears in the record as the most accurate of the assistants. He also had the advantage of assisting Prof. Boys in his delicate experiments with the radio-micrometer, in timing the periodicity of the electric discharge, and in photographing the flight of bullets. In the meantime, he was occupied with J. W. Rodger on an elaborate investigation of the magnetic rotation of the plane of polarisation of light in liquids ('Phil. Trans.,' 1895), which has not yet been surpassed. He next undertook a research by an original method on the determination of the earth's magnetic field ('Phil. Trans.,' 1902, pp. 431–462), which threw light on some important sources of error in most absolute magnetic measurements. He continued to take a great interest in terrestrial magnetism, and designed an ingenious and original set of self-recording magnetographs, which have been employed at Kew, Eskdalemuir, and other observatories, and have proved to be most accurate instruments for recording small variations, especially of the vertical force.

While engaged in these researches, and taking a full share of the teaching work, Watson yet succeeded in finding time to write his well-known 'Text-book of Physics,' which has passed through many editions, and was followed later by his 'Intermediate Physics,' and 'Practical Physics.' These books have made his name familiar to a large circle of students, and have become deservedly popular in other countries.

He took a large share in the design and equipment of the new laboratory to which the Physics Department of the Royal College of Science was transferred in 1905, especially in regard to the magnetic laboratory, and to the building designed for motor testing, in which he had become greatly interested. He was one of the first and most indefatigable members of the Expert and Technical Committee of the Royal Automobile Club, and of the Committee of the British Association on gaseous explosions. In pursuance of this work he designed a modification of the diaphragm type of optical indicator, by introducing a separate mirror for the piston motion, which converted the device into an instrument of accurate scientific research, affording a notable advance on previous methods, especially at high speeds. With the aid of these intruments, and other specially designed equipment, he was able to investigate the performance of a high-speed motor with a precision previously unattainable, and made many valuable contributions to the scientific development of the petrol motor, which have since found a place in most standard treatises on the subject.

Watson assisted Sir W. de W. Abney for many years in his experiments on colour vision, and made useful contributions of his own to the theory and methods of measurement. A characteristic example will be found in his paper on luminosity curves ('Roy. Soc. Proc.,' vol. 88A, p. 404, 1913). He was busily engaged on some promising developments of this work at the time when war was declared.

Soon after the outbreak of the war, the Physics Department of the Imperial College was asked to assist in solving a great variety of problems presented by new methods of scientific warfare. This became so acute with the advent of poison-gas in April, 1915, that Watson was despatched to France to experiment with defensive measures in the trenches. The first experiments by any of the Allied Armies on a gas-cloud in the field were made under Watson's direction in May, 1915. The Central Laboratory was definitely established, with Watson as director, in June, 1915, and played a very important part in the practical evolution of protective devices, which finally made the British Army the best protected from gas among all the belligerents.

The defensive measures against poison-gas soon entailed the systematic collection and examination of all kinds of German shell and fuses. The Germans naturally made this work as difficult and dangerous as they could, and Watson took the keenest delight in the manipulative skill with which he succeeded in circumventing their devices. In cases of exceptional danger, he always insisted on taking the risk himself. According to an American eye-witness, he went out on one occasion into "no man's land" to dig up a "dud" shell under fire, when it was urgently necessary to find out what kind of gas the Germans were using. From the intimate practical knowledge thus acquired at great personal risk, he soon became the leading expert on German ammunition, of which he collected a unique museum for instructional purposes. Owing to his sound judgment and wide practical experience, his advice was eagerly sought by all branches of the service on all kinds of other scientific problems too numerous to mention. This work was of great value, but the examination of gas-shell and the testing of protective devices remained the most hazardous and exacting of his duties. In spite of all reasonable precautions, he was frequently "gassed" with a variety of poisons, under the combined effects of which his health ultimately broke down. He might have recovered if he had been willing to stay a few more days in hospital under medical advice at a critical juncture. In the last great gas attack, when the Germans so nearly succeeded in reaching the coveted coast of Calais, who can say that Watson's utter devotion to duty may not have been one of the straws that turned the scale.

H. L. C.

JAMES EMERSON REYNOLDS, 1844–1920.

James Emerson Reynolds was born at Booterstown, co. Dublin, on January 8, 1844. He was the son of Dr. James Reynolds, a medical practitioner at Booterstown, a man of some literary ability and the author of one or two plays which had a certain measure of success. His mother, originally a Miss Campbell, was English. He was named after his great uncle, a Captain Emerson, of the Royal Navy.

Emerson Reynolds, as he was usually called, was intended for the medical profession, and in early youth became an assistant to his father. In 1865 he qualified as a licentiate of the Edinburgh College of Physicians and Surgeons, and afterwards practised for a short time in Dublin; but on his father's death he definitely abandoned medicine, and following a strong inclination, devoted himself solely to chemistry. At Booterstown he had fitted up a small laboratory, and tried his hand at research work from the outset.

He was not a student of Trinity College, and never attended a systematic course of instruction either in theoretical or practical chemistry. In fact, he was wholly self-taught. His first paper, "On the Oleaginous Matter formed on dissolving different kinds of Iron in Dilute Acids," appeared in the 'Chemical News' for 1861, when its author was, presumably, only 17 years of age. In the same year, and in the same volume, appeared a second paper, "On a New Process for Photographic Printing." These were followed, next year, by a communication to the same journal on the "Oxalates of Iron;" and in 1863 by no fewer than five contributions, partly to the 'Chemical News' and partly to the 'Journal of the Royal Dublin Society.' Their various subjects—"On the Economical Preparation of Sulphocyanide of Ammonium" ('Chem. News,' vol. 8, p. 14, 1863); "On the Numerical Nomenclature of Spectral Lines" (*idem*, p. 59), "On the Detection of Hyposulphite of Soda" (*idem*, p. 283); "Wood Spirit and its Detection" ('Dublin Roy. Soc.,' vol. 4, p. 126, 1863); "Note on Pure Methylic Alcohol" (*idem*, p. 131)—if of no special merit or great originality, are, at least, remarkable as the work of a self-taught youth, wholly unguided, and with very limited means. They serve to show the range of his activities, and the assiduity with which he followed the developments of contemporary science. Spectrum analysis was only in its infancy in 1863. Reynolds' practical interest in the subject was probably quickened by the popular lectures of the late Sir Henry Roscoe and Sir William Huggins to the Royal Dublin Society, and, as subsequent papers show, he maintained this interest to the end of his days. His early work was carried on under considerable difficulties, and as it was probably regarded as an interruption to his medical studies, it is doubtful if it received much encouragement at home. It was not until 1867, when he became keeper of minerals at the National Museum in Dublin, that he had access to a fairly equipped chemical laboratory. The subject-matter of many of his papers from 1868 onwards—*e.g.*, formation of dendrites, manganese ores, phosphoric acid in minerals, classification of silicates, notes on Irish rutile and the felspars, boron minerals, mineralogical tables, etc., etc.—may be said to have had their origin in this appointment; and it was probably due to the interest thus created in the chemistry of silicon, which he laboured to show was conceivably co-extensive with that of carbon, that we owe his many papers on the silicic acids, silicon haloids, and on silico-organic compounds, which he continued to publish, from time to time, down to his last paper in 1913.

To this early work belongs his discovery of the colloidal derivative of mercury and acetone ('Roy. Soc. Proc.,' vol. 19, p. 431 (1871)), which originated from his experiments on wood-spirit. It was the first colloidal derivative of mercury to be made known. The neutral solution of the compound $(C_3H_6O_2).3HgO$, prepared by dialysis, was used with success by the late Sir Charles Ball as an antiseptic dressing in surgery, where no ordinary mercurial solution could be used.

In 1868 he became analyst to the Royal Dublin Society, and two years later was appointed Professor of Chemistry at the Royal College of Surgeons, Dublin. He held both these positions until his election, in 1875, to the Chair of Chemistry at Trinity College, Dublin, as successor to Dr. James Apjohn. At this period Reynolds had a considerable practice as a consultant and public analyst. He was interested in subjects relating to medical chemisty and hygiene, and had collaborated in the production of a "Manual of Public Health for Ireland." He was responsible for the analytical examination of the Vartry water as supplied to Dublin, and had laboured, like many before and since, at the perennial question of the utilisation of Irish peat.

On his appointment to Trinity College, Reynolds devoted himself, almost exclusively, to the duties of his chair. He was a good lecturer and an excellent teacher, somewhat precise in manner and diction, and too strict a disciplinarian to be generally popular with the type of student he had to teach. But he always commanded the respect of his pupils, who could appreciate the care and thought he spent on his lectures. They were always admirably illustrated by experiments, for he spared no pains in acquiring or devising suitable and striking demonstrations. If an experiment failed, which rarely happened, he insisted on its successful repetition on the next occasion. He was scrupulously careful that his teaching should be abreast of contemporary knowledge. He early perceived the significance and value of the doctrine of Periodicity, and his course of instruction was arranged in conformity with it. His theoretical conceptions of the basic principle of the Law, afterwards expanded by Sir William Crookes, and his graphic and glyptic representations of it are well known to teachers of chemistry. He was among the first to attempt to settle the true position of the element glucinum in the periodic series, and to establish its valency and atomic weight. It is true that the experimental proof he was able to adduce was not wholly convincing, as the metal which he had himself prepared was far from pure, and the foreign matter present introduced a very uncertain correction. It was only subsequently established that the specific heat of glucinum, as in the case of other elements of low atomic weight, varied very rapidly with the temperature, and that it was only at comparatively high temperatures that the value of its atomic heat approximated to that demanded by Dulong and Petit's law—a fact which accounted for the discrepant conclusions of previous and subsequent workers. Nevertheless, Reynold's prevision of the true place of glucinum in the periodic series turned out to be correct, and there is no further doubt on the subject.

Reynolds was one of the first to introduce quantitative work into the early training of the student of chemistry, thereby familiarising him experimentally with the relation between atomic weights, equivalents, valency, etc. His 'Experimental Chemistry for Junior Students,' in which he developed this system, was a distinctly original work, and has had a considerable measure of success in school teaching. As his own staff was very limited, much of his time during the session was spent in doing demonstrator's work in the laboratory. In this way he acquired practical experience of the working of his system, which he incorporated in subsequent editions of his book. Indeed, he gave so much of his time and energies to his professorial duties that steady uninterrupted research work had to be relegated to the vacations.

Probably the best known of Reynold's contributions to organic chemistry is his discovery of thiourea. As already stated, one of his earliest contributions from the little laboratory he had established when a boy in his father's house at Booterstown was concerned with ammonium sulphocyanide. On heating this salt to a few degrees above its melting point, dissolving the product in water, and allowing the concentrated solution to stand, he obtained a substance crystallising in silky needles, the true nature of which for a time escaped him, but which he eventually characterised as an isomeride of sulphocyanogen, under which title he communicated a short paper to the 'Journal of the Royal Dublin Society.' A further account appeared in the 'Journal of the Chemical Society' for 1869, and was quickly republished in various continental periodicals. It is not often that a young man of twenty-three hits upon so remarkable a discovery, and particularly one which had baffled the skill of men like Liebig and Hofmann. It at once established

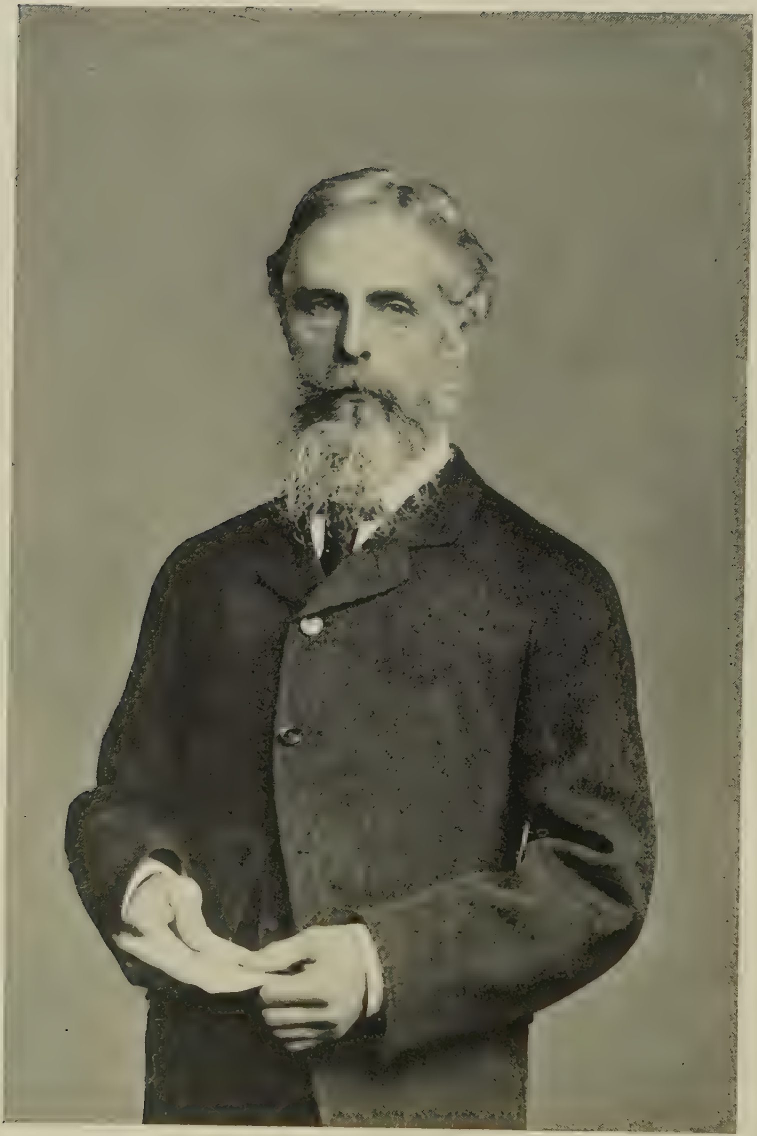
Reynolds' position as one of the most promising of the younger Irish chemists, and no doubt contributed greatly to his subsequent professional success. Thiourea, or thiocarbamide, as it was indifferently termed for a time, proved to be an exceedingly reactive substance, and the preparation of its derivatives and congeners, and the elucidation of their constitution, have been pre-eminently associated with the chemical laboratory of Trinity College, Dublin.

Reynolds vacated his chair in Dublin in 1903, and took up his residence in London. He continued to pursue his experimental work at the Davy-Faraday laboratory, and ultimately fitted up a small laboratory in his house. His last published communication "On the Synthesis of a Silicalcyanide and of a Felspar," appeared in the 'Proceedings of the Royal Society' in 1913. In previous papers he had given descriptions of organic compounds containing the silicocyanogen group, SiN, proving the marked affinity of silicon for tervalent nitrogen. In his last paper he gave an account of the synthesis of a silicon compound of aluminium and calcium—a calcium silicalcyanide, $CaSi_2Al_2$, analogous to CaC_2N_2, yielding on oxidation a substance of the composition of anorthite, $CaAl_2Si_2O_8$, with the properties of the naturally occurring mineral. The keeper of the minerals of 1867 was, up to the last, faithful to the conceptions which had dominated nearly half a century's intellectual activity.

Reynolds joined the Chemical Society in 1873, and became a Vice-President in 1881–4, in 1889–92, and again in 1897–1900. In 1901–1903 he served as President. In the first of his presidential addresses he discussed, with his characteristic lucidity of exposition, the development of a subject to which he had given much thought, and with which he had been associated since the early eighties, viz., the Periodic Law. In the following year he dealt with some pressing questions of inorganic research—inorganic isomerism and the so-called inorganic ferments, in which he gave a highly suggestive summary of many problems which have since occupied the attention of many workers, and some of which have proved to be of great technical importance. He was elected into the Royal Society in 1880, served on the Council, 1900–1902, and was a Vice-President in 1901–1902. He was an original member of the Society of Chemical Industry, of which he became President in 1891, presiding over the only Annual Meeting of the Society held in Ireland. He presided over the chemical section of the British Association at the Nottingham meeting in 1893.

In 1875 he married Janet Elizabeth, the daughter of Prebendary Finlayson, of Christchurch Cathedral, Dublin, who survives him. During his later years his eyesight, never very good, gradually failed, but his mental power was active to the last. He had a serious accident in the autumn of 1919, fracturing a rib; this was followed by a slight stroke, from which he never wholly recovered. He died very suddenly on February 17, 1920, at his residence in Kensington.

T. E. T.



A. V. Harcourt.

A. G. VERNON HARCOURT, 1834–1919.

By the death of A. G. Vernon Harcourt in his eighty-fifth year, there passed away a chemical teacher endeared to many generations of Oxford students, a singularly skilful experimenter, and a pioneer in the new domain of physical chemistry. He was one of the first who planned experiments to follow the course of a chemical change, to measure the velocity of a reaction, and to study the conditions that determine it; he rebelled against the idea that chemists had to concern themselves only with the preparation of new substances and the elucidation of their properties—for him the interesting thing was *how* the change happened, not what was the result.

Augustus George Vernon Harcourt was the elder son of Admiral F. E. Vernon Harcourt and of Marcia, sister of the first Lord Tollemache, and grandson of the Archbishop of York. He was born December 24, 1834, and died August 23, 1919. He was educated on the old classical lines at Cheam and at Harrow, and entered Balliol College, Oxford, in 1854.

It was at Balliol, under Henry Smith, that he laid the foundation of his chemical career. Harcourt, in his reminiscences of the Oxford Museum and its Founders, has told us how, when Salvin's buildings at Balliol were constructed early in the "fifties," two cellars were appropriated to the study of chemistry; and to provide a teacher, Henry Smith, ablest of Oxford men, was deputed by the College to take some lessons in the subject. He went for a few months to Dr. Hofmann at the College of Chemistry. Montgomerie, Hertford Scholar in 1854, and Harcourt were his first pupils. The classical atmosphere of the College cellar is brought out in one of Harcourt's reminiscences: "Once a stick of phosphorus took fire on the bench; Montgomerie was for pouring water over it, which might have caused a dangerous scattering of the fiercely burning liquid; Henry Smith stopped him, and extinguished the blaze by pouring over it a little sand, remarking in his soft tones—'*Pulveris exigui jactu compressa quiescet.*'"

When Brodie, a pupil of Bunsen, came to Oxford as Professor of Chemistry, the Balliol cellars were placed at his disposal, and Harcourt became first his pupil and then his assistant. At Balliol, Brodie began working on the peroxides of the acid radicals, and afterwards on the oxidation of graphite, and then turned to the systematic study of the alkaline peroxides, whose reducing action he was the first to explain—incidentally supplying a strong *chemical* argument in favour of the diatomic nature of oxygen gas. In 1858, Brodie migrated to the chemical department of the New Museum, and took Harcourt—still an undergraduate—with him as lecture assistant. A year later, after gaining a First Class in the School of Natural Science, Harcourt was appointed Demonstrator in the Students' laboratory, known from its prototype as the "Glastonbury Kitchen"—and among his first pupils was the Prince of Wales, afterwards King Edward VII.

Under Brodie, at the New Museum, Harcourt began his researches with the exact determination of the oxygen absorbed by the metals potassium and sodium—allowing air to enter slowly into a flask containing the pure liquid metal heated in an atmosphere of nitrogen. In this first paper one can see that it is the initiation and progress of the oxidation that interest him. "Soon after the dry air has begun to mix with the nitrogen, the grey film which covers the molten metal changes to a deep blue; the surface gradually becomes roughened by little wrinkles and projections, and a moment arrives when a single spluttering spark appears at one point and a dust of white oxide rises. . . . . At the point where the spark appears the blue crust becomes white, and this change passes in a moment over its whole extent."

In 1859 Harcourt was elected Lee's reader in chemistry and a senior student of Christ Church, but it was not until some years after his appointment that he began his work in the Lee's Laboratory. Meanwhile he had started those researches on the rate of chemical change which—in conjunction with those of Berthelot in France and those of Guldberg in Norway—were to establish on a quantitative basis Berthollet's law of mass action. In the interpretation of his results Harcourt was associated with William Esson, whose special mission in Oxford seemed to be—as the writer knew him—to illuminate mathematically the obscure records of chemical velocities. Harcourt and Esson first studied the reaction between oxalic acid and potassium permanganate in acid solution. They found that the rate of change varied with the amount of manganous sulphate formed, and that the reaction was probably *nil* in the complete absence of manganous salt; but, once started, the velocity would increase to a maximum and then fall off—the curve representing the course of the change having a point of contrary flexure. They liken their curves to those obtained by Bunsen and Roscoe in the course of photo-chemical induction—thus suggesting that the "inductive period" in the union of hydrogen and chlorine was due to the action of another substance, a suggestion which finally was proved to be correct.

Seeking for a less complicated reaction, Harcourt found that in dilute solutions hydrogen peroxide decomposed hydrogen iodide with velocities that could be easily followed, and the amount of change could be accurately ascertained. The method of carrying out the experiment in a stream of carbon dioxide, and the device by which the iodine liberated was reconverted into iodide by the successive additions of exactly equal drops of concentrated thiosulphate, show Harcourt at his best as an experimenter. The time-intervals between the successive appearances of the iodine proved that the velocity of the change varied directly with the quantities of each of the reacting substances—when the other conditions were kept constant. The rates found, however, do not prove that the change is necessarily a trimolecular one as Harcourt supposed:—

$$H_2O_2 + 2HI = 2H_2O + I_2.$$

The change most probably takes place in two stages, each of which is di-molecular; but, one stage being much faster than the other, the observed rates follow the simple law. In studying the effect of temperature on the rate of this reaction Harcourt and Esson arrived at a zero of chemical action in wonderful agreement with the absolute zero calculated from physical data.

Harcourt was so strongly convinced that chemical change followed mechanical laws that his laboratory became a centre where the experiments of Bunsen and his school on "chemical induction" and "sprungweise" explosions were repeated and criticised.

Though one of the pioneers of physical chemistry Harcourt remained a sceptic towards the new theories of solution and ionisation, and the word "dissociation" was anathema to him. In his last address as President of the Chemical Society in 1897 he maintained that the distinction between dissociation and decomposition was absurd. "A journey" he declared "is the same journey, whether I go with a return ticket, or whether I cannot return by the same route."

Of the painstaking character of Harcourt's demonstrations, of his insistence on neatness and cleanliness, of the patience and personal trouble he took with each beginner, generations of old Christ Church men can speak with grateful appreciation. The minutiæ of manipulation appealed to him, but they were only means to attack the largest problems; for him no defect was too small to remedy, no authority was too great to question. Through the inspiration of his example and teaching Oxford, no less than English chemistry, has been intellectually quickened.

In applied chemistry Harcourt was chiefly drawn to questions dealing with the purification and testing of coal-gas, he having been appointed in 1872 one of the three Metropolitan Gas Referees whose duty it is to prescribe the mode of testing the London gas and, subject to the various Acts of Parliament, to fix the limits of impurity allowed. One of his early researches on coal-gas was his attempt to purify the gas from sulphur compounds by means which he devised for converting the carbon disulphide into hydrogen sulphide. Harcourt's "sulphur test" came into wide use, but its application on a large scale for the purification of coal-gas has only recently been carried out successfully by Dr. Charles Carpenter at the South Metropolitan Gas Works. Perhaps the most signal improvement in the testing of gas effected by Harcourt was the introduction of the Pentane Lamp as the official standard of light in place of the variable spermaceti candle. His original one-candle lamp has been replaced by the more convenient 10-candle Pentane lamp, and this has been largely adopted as the measure of illuminating power not only for gas but for other illuminants.

Another very useful investigation which occupied much of his time between 1899 and 1911 was concerned with the administration of chloroform as an anæsthetic. Already in the former year he had devised a ready means for determining the percentage of chloroform vapour, mixed with air, by converting the chloroform into carbon dioxide and hydrogen chloride in contact with a red-hot platinum wire in presence of steam and of water to absorb the hydrogen chloride:—

$$2CHCl_3+2H_2O+O_2 = 2CO_2+6HCl.$$

When the Council of the British Medical Association in 1901 appointed an expert committee to investigate the methods in use for administering chloroform, to study its quantitative determination, and "to determine if possible what is the minimum dose which would secure anæsthesia for operations and at the same time not endanger life," they gave their committee power to co-opt two outside members—of whom Harcourt was their first choice.

After much patient labour he devised an "Inhaler" which his colleagues described as "possessing the advantages of simplicity, exactness and portability." The Committee adopted it in their experiments, and in their final Report state that it appears to be well adapted for universal employment.

Of recognition by learned societies and of devoted service rendered to them Harcourt could claim a large share. Elected to the Royal Society in 1863, he served on the Council 1878—80. In conjunction with Esson, he published four memoirs in the 'Philosophical Transactions,' in the third of which, the Bakerian Lecture for 1895, the observations are given indicating that all chemical action would cease at $-272{\cdot}6°$ C.

Admitted to the Chemical Society in 1859, he served as one of its Secretaries for eight years 1865—73, and was elected President in 1895. In 1910 he was one of the five Past-Presidents whose jubilee as Fellows was celebrated by the Society.

As became the nephew of one of the founders of the British Association —Rev. W. Vernon Harcourt—he early took an interest in its meetings and made many contributions to the Chemical Section, of which he was President in 1875. A few years later he was elected one of the General Secretaries of the Association, an office he held for fourteen years with conspicuous tact. He was an honorary Doctor of Oxford, McGill, and Durham Universities.

In 1872 Harcourt married Rachel Mary, daughter of Mr. H. A. Bruce, at that time Home Secretary in Mr. Gladstone's first administration and afterwards Lord Aberdare. Of his happy family life at Cowley Grange, the home he built for himself on the banks of the Cherwell, many of his old Oxford pupils and friends can tell; and perhaps no more picturesque spot could have been chosen for the evening of his days than St. Clare, near Ryde, the property he inherited, with its fine cedars and beautiful lawns, falling from terrace to terrace down to the waters of Spithead. Even in the sunny Isle of Wight people spoke of the roses of St. Clare—that pleasantest corner of the world of which he would quote when bidding one to an Easter or an autumn visit:

"Ver ubi longum tepidasque praebet
Juppiter brumas."

Both at Oxford and St. Clare, Harcourt displayed extraordinary activity in games. Without being an athlete, he was naturally fond of all sports and outdoor exercises, and, once interested in a game, he took infinite trouble to improve. Many of his pupils found, to their surprise, that their white-haired tutor could give them lessons in other things besides chemistry.

His knowledge of the classics, especially of poetry, and a memory which remained excellent till quite late in life, made him apt at quotation and ready in rejoinder. He was a really good critic of style. Singularly lucid as a writer, he set his pupils an example of precision and clearness, which some, it must be admitted sorrowfully, could not reach, though they tried to follow it.

His life was a full and happy one; he followed the path he had chosen, with never a thought for profit or self-advancement. If he had an ambition, it was the desire to serve others, and to feel that he was loved by his friends.

Few men have been so completely happy in their work, or lived so much in the lives of their students. The writer, whose good fortune it was to fall under his influence at Oxford, gratefully acknowledges that he owes his career to Harcourt's affectionate interest and to his example.

H. B. D.

ETTRICK WILLIAM CREAK, 1835–1920.

Captain Ettrick William Creak was born on the 28th May, 1835, and died in his sleep in his eighty-fifth year on the 3rd April, 1920.

He was the son of the late Commander William Creak, Royal Navy, of Norfolk, and a nephew of Sir H. Havelock, of Lucknow fame. Following his father's profession, he joined the navigating branch of the Navy about the year 1849, and was appointed to a ship on the Australian station, where he was a messmate of the late Admiral of the Fleet, Sir Frederick Richards.

His service afloat as navigating lieutenant was distinguished by his nautical acquirements, and the remarks he sent from time to time to the hydrographer, for which he was specially thanked in 1866. His knowledge of French and music were accomplishments more rare in those days than in these.

During his service on board H.M.S. "Esk" from 1863–1867 he added to our knowledge of various unsurveyed localities on the Australian station, amongst which a plan of Ngaloa Bay, in the Fiji Islands, may be particularly mentioned.

The great range of magnetic latitude traversed by H.M.S. "Esk" turned Lieutenant Creak's attention at this time to an investigation of the errors of the compass arising from this cause, which enquiry was embodied in a report to the Admiralty and published by the Board of Trade. Later, an elaborate discussion by him of the same subject appeared in the 'Philosophical Transactions of the Royal Society,' 1883, part 2.

This was the beginning of Creak's researches in the science of magnetism, and marked him out as a suitable officer to be employed in the investigation of compass errors in H.M. ships, which were being increasingly constructed of iron and steel.

He was accordingly selected, in 1868, to serve as assistant in the Compass Department of the Admiralty.

In connection with the famous "Challenger" Expedition, 1872–76, Lieutenant Creak took an active part in the determination and control of the constants required for the reduction of the magnetic observations that were to be made during the voyage.

The results of the "Challenger" observations are published in vol. 11 of the official narrative of the voyage, and in vol. 11 of the report on the physics and chemistry of the expedition, where plans, constructed by Creak, are given of the magnetism observed at the Bermuda Islands, and also charts of the variation, inclination, horizontal force, and vertical force for the epoch 1880, constructed mainly from the "Challenger" observations, combined with all other observations available to the date of publication.

The instruction of officers engaged in the Arctic Expedition of 1875–76 under Captain G. S. Nares, R.N., was entrusted to Commander Creak. He also prepared the directions and magnetic charts for the 'Arctic Manual,' 1875. Many years later, Captain Creak drew up the magnetic instructions for the Antarctic Expedition of 1901, besides settling the details in connection with the fitting of the magnetic observatory on board the "Discovery."

The appointment of Superintendent of the Compass Branch of the Hydrographic Department of the Admiralty falling vacant in 1887, Staff-Commander Creak was selected for it. The Admiralty compass of that period was excellent in some respects, but complaints were received of its excessive vibration, amounting to almost a revolution when in heavy weather the rolling of the ship synchronised with the swing of the card. Having a heavy and comparatively small card with long needles, it did not lend itself to the correction of quadrantal and healing errors, with the result that, in the types of ships then building, uncorrected errors were necessarily large and liable to great changes, consequent on change of geographical position with varying magnetic elements. The inconvenience inherent in such a form of compass was very irksome, besides being a source of danger.

Sir William Thomson (Lord Kelvin) had already introduced his well-known compass, fulfilling all the requirements that a compass should, except the one essential to ships of war, viz., ability to withstand the shock of heavy gun fire in large ships, and the effects of vibration and rapid motion in small vessels, such as torpedo-boats and destroyers. The new compass was extensively fitted in ships of the Mercantile Marine, for which it was admirably designed, and a strong desire was manifested by naval officers to be supplied with it.

The defects of the Admiralty compass were fully realised by Captain Creak, and the advantages of the new compass were not less appreciated by him, but he also recognised the fact that a compass that would fail in battle was not one that should be fitted on board H.M. ships if it were possible to devise a compass free from that fatal defect, and at the same time be equally good as Sir William Thomson's compass in other respects.

With this object in view, Creak set himself to develop the existing liquid compass, feeling confident that in the principles of that compass lay the solution of the problem. The existing liquid compasses, which had up to that time been looked upon only as subsidiary types for use in rough weather and during gun firing, were, owing to defects in the general principles of construction, far from being reliable instruments under ordinary seagoing conditions. The cards were floatless, with large moments of inertia and the weight resting upon the pivot was excessive, necessitating powerful needles with large magnetic moments in order to overcome the sluggishness resulting from the inertia, skin friction of the liquid, and the friction between the cap and pivot.

He introduced cards mounted on a float, with two thin and relatively short needles, fitted with their poles at the scientifically correct angular distances, and with the centre of gravity, centre of buoyancy and the point of suspension in correct relation to each other. The flotation and the total weight were so adjusted to one another as to reduce the weight resting on the pivot to a reasonable amount, being considerably less than the Thomson dry cards, and at the same time sufficient to prevent the card from "pumping" when subjected to vertical shocks or vibration. He was thus able to use iridium pointed pivots instead of the relatively blunt ruby pointed pivots which had hitherto been necessary owing to the excessive weight which they had to carry. An improved form of azimuth circle was at the same time introduced.

The compass thus designed rectified the defects of the Admiralty Standard compass, referred to above, with the additional advantage of considerable steadiness under heavy gun-fire and in a seaway, but Creak had to patiently face great and ignorant obstruction—official and other—before he succeeded in getting this compass installed.

Certain modifications have been introduced at various dates, but the main features of practically all these improvements still obtain in liquid compasses at the present time.

Meanwhile, the demand in the Naval Service for Lord Kelvin's compass was growing strongly, and in 1892 the Board of Admiralty decided that the change should be made without waiting longer for the further developments that Captain Creak hoped to be able to effect. The liquid compass in the stage it had then reached fulfilled all essential conditions, and particularly steadiness under gun-fire and in a heavy seaway; but it had to be admitted that for manœuvring purposes it was inferior to Lord Kelvin's compass, owing to comparative sluggishness on a large alteration of course through the drag on the card by the liquid in which it floated.

Superintendent of Compasses was strongly supported by the Hydrographer in his view as to the possibilities of the liquid compass, and time and opportunity were pressed for to remove its one admitted defect before taking the momentous step of changing the compass equipment for the whole Navy.

Unfortunately, the Hydrographer was unable to impress his views on the Board, and the change was made. The Kelvin compass was at that time by no means such a perfect instrument, within its limitations, as it became later on, and when its adoption by the Admiralty was decided upon, Captain Creak dropped further development of the liquid compass, and devoted himself whole-heartedly to the improvement of the Kelvin.

As subsequent events proved, the decision taken by the Admiralty was unfortunate, because it not only took away from the Compass Department the incentive to further effort, but also lost the advantage of securing the co-operation of navigating officers afloat in seeking a remedy for its single defect, all attention and interest being now concentrated on the Kelvin compass. The liquid compass was, however, retained for use on board small craft, for which the other was manifestly altogether unsuitable.

Sixteen years later Creak's views were justified. As the size of guns increased and the development of modern battle practice progressed, the need of an efficient compass in such conditions could no longer be ignored, and the Kelvin compass was found to be quite unsuitable for naval purposes in war. The neglected merits of the liquid compass gradually became recognised, and numerous requests for auxiliary liquid compasses were received at the Admiralty.

Early in this century, Mr. D. Buckney, of Messrs. E. Dent and Co., when designing a liquid compass for the use of submarines, conceived the idea of slightly diminishing the diameter of the card, associated with a projecting lubber point. During the trials, the effect of this slight modification was found to be equally unexpected as it was extraordinary. It was apparent that the drag on the card system was thereby reduced to a minimum, and its defect as a manœuvring compass was practically cured. Further improvements rapidly followed, the result being patented under the name of the "Chetwynd" compass, and in 1908 the triumph of the liquid compass was complete, and it was introduced generally throughout the Navy.

The foundation of this great success was laid by Captain Creak, and credit for the years of experiment and research that he spent on developing the principle of the liquid compass must be his, no less than the tenacity with which he held to his opinions, based as they were on a correct appreciation of the requirements of the Navy as distinct from those of the Mercantile Marine. The merit of hitting on the remedy that had baffled him belongs, however, to another, and no one rejoiced more heartily at his success than Captain Creak.

A simple form of instrument for the correction of the heeling error by magnets was devised by Captain Creak, and he also invented the Lloyd-Creak dip and intensity apparatus, originally meant for observations afloat, but which has been found very useful also on shore. The heeling error instrument has other applications besides that for which it was originally designed, and is extremely useful for the determination of vertical force both afloat and ashore. The Lloyd-Creak instrument was fully described in 'Terrestrial Magnetism' for October, 1901.

For his various contributions to the science of magnetism, Captain Creak was elected a Fellow of the Royal Society in 1885, and served on the Council from 1898 to 1900. From time to time, papers were read by him at the Royal Society on subjects connected with magnetism on board H.M. ships and the discussion of the results of magnetic observations, made in the course of voyages by H.M. surveying vessels and expeditions such as those of the "Challenger" and the Arctic Expedition, 1875–76, which papers appeared in the 'Philosophical Transactions' and the 'Proceedings' of the Royal Society.

Of Captain Creak's other writings, he assisted the late Sir F. Evans and Mr. Archibald Smith in preparing and publishing the "Elementary Manual for the Deviation of the Compass in Iron Ships" in 1870, and, after the death of Sir F. Evans, later editions of that manual were entirely prepared and published by Captain Creak. In the ninth edition, prepared by him in 1895, the question of heeling error and its correction were specially discussed, and tables were given to assist in the correction of quadrantal deviation and the application of the Flinders' bar.

He also assisted in writing the article on "Terrestrial Magnetism" in the 'Admiralty Manual of Scientific Inquiry,' and was the author of the article in the 'Encyclopædia Britannica,' 10th edition, on "Compasses."

Other of his works published included "The Mariners' Compass in Ships of War," "Compass Correction in Iron Ships," and discussion of the subject from the time of Flinders (early Nineteenth Century) and containing a comparison of the Thomson and Peichl methods.

It was pointed out by Captain Creak that at certain positions in the world magnetic areas exist which affect the compasses of vessels sailing over those areas, and he deduced a law which appears to hold good governing the deflection of the needle in relation to the magnetic axis of the disturbed area in the two hemispheres.

One striking instance of large deflection occurs in an area near Cossack, in North Australia, which on being crossed by H.M. Surveying Vessel "Meda" in a depth of 8 fathoms, with two shore objects in transit, deflected the compass needle 30° for about one mile. The magnetic conditions over this area were carefully observed by Commander (later Vice-Admiral) W. U. Moore, in H.M.S. "Penguin," and they were discussed by Captain Creak in a paper read at the Royal Society.

At Funafuti, a coral atoll in the Pacific, in lat. 8° 30′ S., long. 179° 12′ E., another magnetic field exists where the variation differs nearly 2° and the dip 1° in different localities, as shown by the magnetic survey of the atoll made by Captain (now Admiral) Sir A. M. Field, K.C.B., in H.M.S. "Penguin" in 1896, the results being investigated by Captain Creak and published by the Royal Society in 1904.

When, owing to his having reached the age of 55, he had to retire from the active list of the Navy in 1891, not having served the number of years to entitle him to be retired with the rank of Captain, a Special Order in Council was issued giving him that rank, so that his important services in the Compass Department should not deprive him of the honour he would have received had he served the requisite number of years at sea. He was made a C.B. in 1901, in which year he was retired from the Compass Department, at the age of 66.

In 1903, he was President of the Geographical Section of the British Association, and in his Presidential Address at Southport in that year gave an interesting account of the progress of our knowledge of Magnetism, both afloat and ashore up to that time. This was published in the Report of the British Association, and also in the 'Geographical Journal,' vol. 22, 1903.

Captain Creak married in 1867 Grace Mary, daughter of W. B. Bradie, Esq., who pre-deceased him, and he leaves two sons and one daughter. He was the most modest and unselfish of men, a staunch friend, broad-minded, and full of charity to all. For many years he was a member of the Council of the Royal Naval Benevolent Society, in which he took an active part up to the time of his death.

His whole heart and soul was in the service and his Department, with not a thought of reward or benefit to himself. High-minded and straightforward and true to the core, he died regretted by all who knew him.

A. M. F.

CHARLES EDWARD GROVES. 1841–1920.

Though during the last twenty years of his life the figure of C. E. Groves was less familiar than formerly in scientific circles, no one was better known and esteemed during the long period in which he held office as Editor of the 'Journal of the Chemical Society.'

Groves was born at Highgate on March 4, 1841, but while still a young child his parents removed to Kennington, and in that neighbourhood he remained until the end of his life. He was educated at Brixton College School, and subsequently entered the Royal College of Chemistry under Hofmann, the first professor.

In October, 1862, he became chief private assistant to Dr. John Stenhouse, F.R.S., who had a laboratory for research in Rodney Street, Pentonville. This was an almost unique establishment. Stenhouse had been for some years lecturer on chemistry at St. Bartholomew's Medical School, but about the year 1856 he had been disabled by a paralytic stroke, from which he partly, but never wholly, recovered. His interest in chemical investigation prompted him, notwithstanding his crippled condition, to resume his researches into the nature of the crystalline constituents of lichens and other vegetable materials, and he found premises to suit his purpose in an old house to which was attached the outbuildings of an abandoned artificial flower factory.

Here, early in 1860, he established himself with E. J. Mills (afterwards professor in Glasgow) as his scientific assistant. Mills was succeeded in Stenhouse's laboratory by C. E. Groves, together with W. A. Tilden as junior. When the latter left, for a post at the Pharmaceutical Society, he was succeeded by R. Meldola (afterwards President of the Chemical Society) and T. Bolas. The little laboratory was always busy, and Groves remained in command until the death of Stenhouse in 1880.

During the later years of this association the papers resulting from the work done were published in the joint names of Stenhouse and Groves, and related almost entirely to products from the lichens and their derivatives. Both were men of earnest religious convictions, and the "Doctor," who could only sit and watch operations, was much disposed to talk during work, which was not unfrequently interrupted by controversy on subjects connected with their respective religious views, Stenhouse being a Presbyterian and great admirer of the famous preacher, Charles Spurgeon, while Groves, as a high churchman, stood up for the episcopal establishment.

The most notable piece of work done by Groves independently was the discovery of the action of zinc chloride in the production of ethyl chloride and its homologues (' Chem. Soc. Journ.,' vol. 12, pp. 636–641 (1874)).

In 1865 Stenhouse succeeded Hofmann as one of the external Assayers to the Royal Mint, and held the office until it was abolished by Mr. Robert

Lowe in 1870. Stenhouse, of course, was incapable of any sort of manipulation, and the work was done by Groves with the aid of a technical assistant.

In 1877, when the Institute of Chemistry was founded, Groves took an active part in the movement and was appointed Secretary; from 1887 to 1892 he was also Registrar. He was connected with the 'Journal of the Chemical Society' from 1878, first as Sub-Editor, and in 1884 as Editor, in succession to Mr. Henry Watts. This office he resigned in 1899. Groves was a good manipulator and skilful analyst. His familiarity with several languages and his extensive knowledge of physical and chemical science were valuable qualifications for the post of Editor, though he may perhaps be remembered for certain peculiarities of phraseology in English on which he insisted and which sometimes brought him into conflict with less scrupulous writers. Soon after Dr. Stenhouse's death in 1880 Groves was appointed Lecturer on Chemistry and Dental Metallurgy in the Medical School at Guy's Hospital, retiring in 1901. For more than twenty years he was also consulting chemist to the Thames Conservancy Board, and gave up this work in 1909. For only a few years later he was able to sustain his interest in scientific work, but failing health compelled him to retire from active life or study, and he died at his house on Kennington Green, February 1, 1920.

Groves became a Fellow of the Royal Society in 1883.

In early life he was a good walker, and though in frame very spare, he was both muscular and active. Though not addicted to games, he found his recreation in mountaineering, and for many years his summer vacations were spent in Switzerland. He will be remembered by many among the older members of the Alpine Club.

W. A. T.

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